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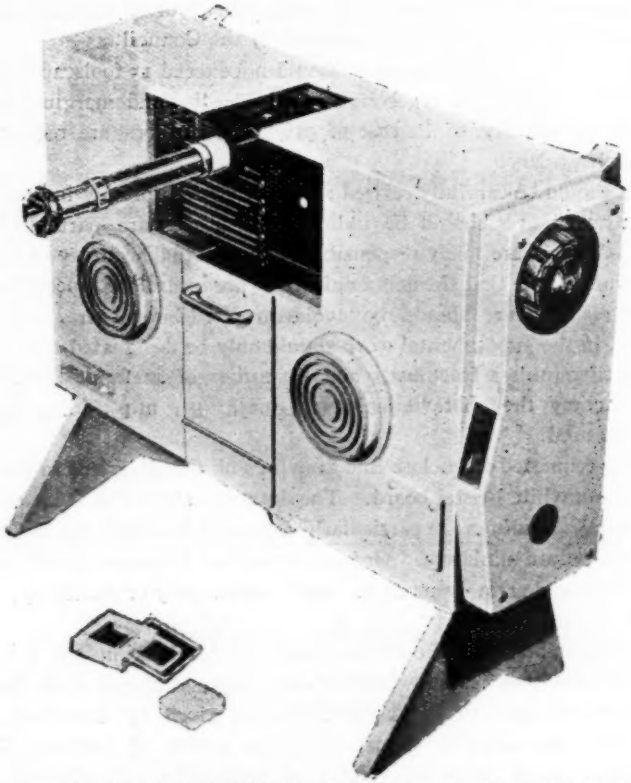

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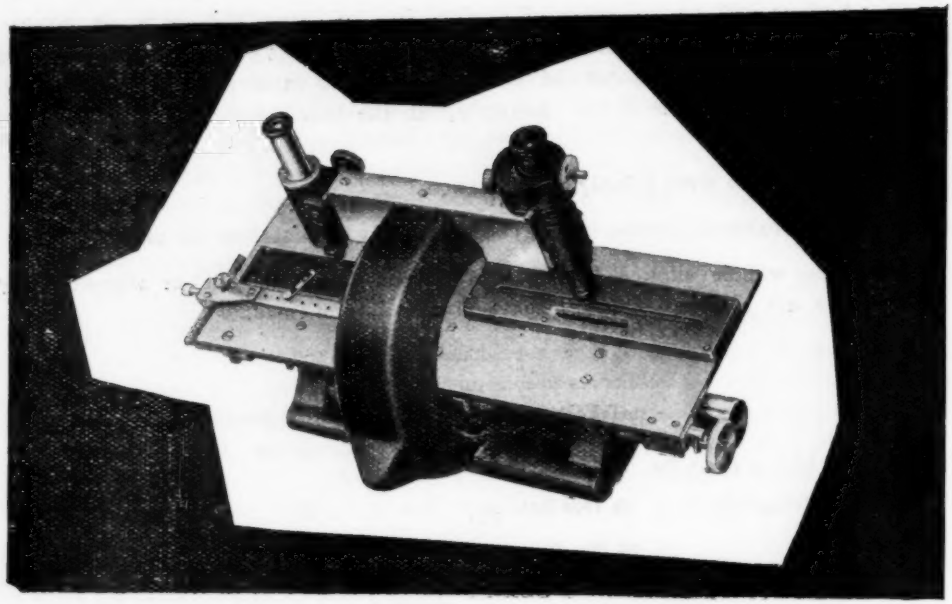

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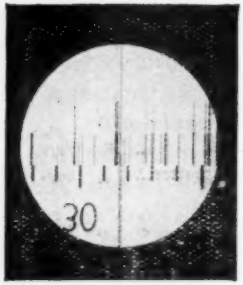

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[Jour. Indian Chem. Soc., Vol. 36, No. 12, 1959]

JUSTIFICATION OF CERTAIN EQUATIONS ON COAGULATION OF COLLOIDS ON THEORETICAL GROUNDS

By B. N. Ghosh and Arun Kumar Gangopadhyay

Reasons have been advanced to justify the assumption that for slow coagulation, ε, in the Smoluchowski equation

$$\Sigma n = \frac{n_0}{1 + \frac{t}{T}\varepsilon}$$

varies with time according to the expression :

$$\varepsilon = \frac{K}{1 + at}.$$

Experimental evidence in support of this equation has been recorded. It has also been shown how Bhattacharya's empirical equation connecting c, the concentration of the added electrolyte with the time, t, of coagulation, can be derived from Reerink's equation which has got a theoretical basis.

Kinetics of Coagulation

In a previous paper the derivation of an equation on the kinetics of slow coagulation of colloids, based on the assumption that ε in the Smoluchowski equation*

$$\Sigma n = \frac{n_0}{1 + \frac{t}{T}\varepsilon}$$

decreases with time, has been reported. Justification of this assumption can be found on the basis of the following reasoning. In the region of slow coagulation the amount of electrolyte added to the colloid is small, and therefore the thickness of the electrical double layey $1/k$ will be large compared to the radius γ of the particles. It has been shown by Verwey and Overbeek ("Theory of the Stability of Lyophobic Colloids", pp. 176-78) that under such conditions the energy of repulsion V_R and consequently the stability ratio, W, increases with the particle radius γ. An examination of the theoretical curve recorded by them shows that the relationship is practically linear within the range of particle radius $10^{-6.5}$ to 10^{-5} cm. It may therefore be reasonably assumed that as the energy of repulsion and, hence, the stability ratio increases, the percentage of successful collisions (*i.e.*, collisions leading to aggregation), represented by ε, decreases.

Therefore, we may write

$$\varepsilon \propto \frac{1}{W} \propto \frac{1}{\gamma}$$

* n_0 = number of particles per c.c. at time, $t = 0$;
Σn = the total number of particles per c.c. at time t, and T is a constant.

Again the average particle size 'γ' increases with the progress of coagulation as Σn decreases. Had there been no decrease in the percentage of successful collision, the Smoluchowski equation,

$$\Sigma n = \frac{n_0}{1 + \alpha \frac{t}{T}},$$

where α is a constant, should have held good.

Therefore, as an approximation we may write

$$\varepsilon \propto \Sigma n \propto \frac{n_0}{1 + \alpha \frac{t}{T}} \quad \text{or} \quad \varepsilon = \frac{K}{1 + at},$$

where K includes n_0 and the proportionality constant, and a represents α/T.

In the present paper we shall record further experimental evidence in support of the equation for slow coagulation

$$\frac{\Sigma n}{n_0} = \frac{(1 + at)}{(1 + \beta t)} \qquad \ldots (1)$$

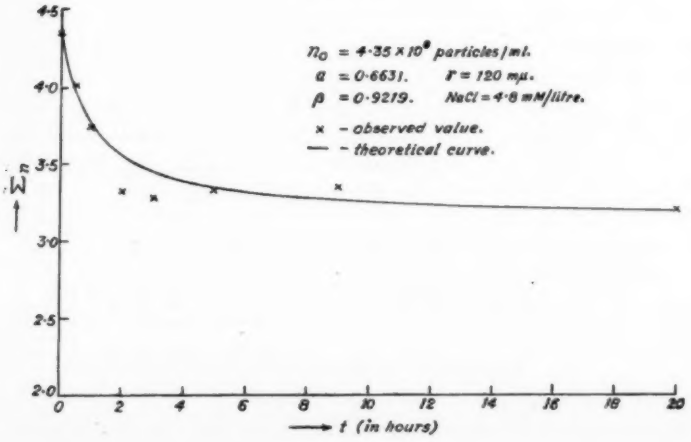
derived previously by one of us (Ghosh, this *Journal*, 1958, **35**, 9) on the assumption that variation of ε with time can be represented by the equation

$$\varepsilon = \frac{K}{1 + at}.$$

Experimental Data and their Interpretation

In the region of slow coagulation ultramicroscopic countings at different intervals of time of particles of selenium sols were made by Kruyt and Van Arkel (*Kolloid Z.*, 1923, **32**, 29) and of a gold sol by Westgren (*Arkiv Kem. Min.*, 1918, **6**, 7). These are represented in the Figs. 1-3 in which each of the arithmatical

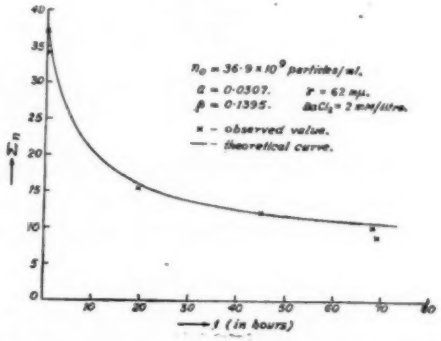
FIG. 1
Gold sol.



number in the ordinate multiplied by 10^9 represents the value of Σn for the selenium sols. Similarly for the gold sol each number in the ordinate multiplied by 10^8 represents Σn. The continuous curves in the figures were drawn on the basis of equation (1) using the values of the constants α and β as recorded therein. The crosses represent the observed values of Σn.

FIG. 2

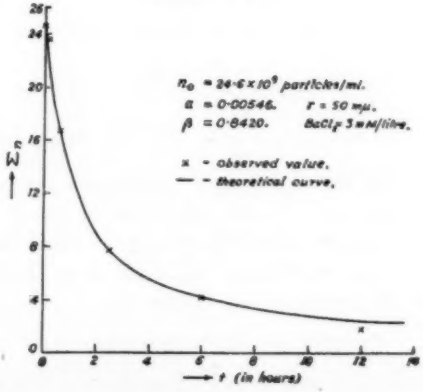
Selenium sol.


$n_0 = 36{\cdot}9 \times 10^9$ particles/ml.
$\alpha = 0{\cdot}0507.$ $r = 62$ mμ.
$\beta = 0{\cdot}1395.$ $BaCl_2 = 2$ mM/litre.
× - observed value.
— - theoretical curve.
Σn
t (in hours)

It will be noticed that the theoretical curves fit the experimental data in a fairly satisfactory manner. In the case of the selenium sol, represented by Fig. 3, after 6 hours, the aggregates consist of six primary particles on the average. Obviously there are some aggregates which contain more than this number and these will tend to settle down and enmesh other smaller particles in this process. Besides this, the thickness of the double layer may no longer be small compared to the particle radius. Hence, from this point onwards the agreement between the calculated and experimental values of Σn is not likely to be satisfactory. In the case of gold sol (Fig. 1) it will be noticed that the concentration of the added electrolyte is such that after the first four or five hours further aggregation of the particles is almost completely arrested.

FIG. 3

Selenium sol.


$n_0 = 24{\cdot}6 \times 10^9$ particles/ml.
$\alpha = 0{\cdot}00546.$ $r = 50$ mμ.
$\beta = 0{\cdot}8420.$ $BaCl_2$ 3 mM/litre.
× - observed value.
— - theoretical curve.
Σn
t (in hours)

Concentration of an Added Electrolyte and its Effect on the Time required for Coagulation

Bhattacharya *et al.* (this *Journal*, 1951, **28,** 179; *J. Colloid Sci.*, 1955, **10,** 551) have proposed an empirical equation connecting the concentration, c, of an electrolyte with the time of coagulation, t, of a colloid. This equation can be expressed as

$$\frac{1}{c-a} = \frac{nt}{m} + \frac{1}{m} \qquad \ldots (2)$$

where a, m and n are constants. In a number of publications (this *Journal*, 1951, **28,** 638; 1952, **29,** 687) they have shown that their equation agrees well with experimental data.

Reerink ("Colloid Science", Vol. I, 1952, edited by Kruyt) has derived an equation connecting the stability ratio W of a colloid with the concentration and valency of an added electrolyte, starting from the equation (*loc. cit*).

$$W = 2\int_{2}^{\infty} e^{v/kT} \cdot \frac{ds}{S^2} \qquad \ldots (3)$$

An approximate evaluation of the integral leads to the expression

$$W = \frac{1}{2\kappa a}\ e^{Vm/kT} \qquad \ldots (4)$$

where κa represents the ratio of the particle radius, a, to the thickness $1/\kappa$ of the double layer, V_m, the maximum value of the energy of interaction in the curve plotted with $e^{v/kT}$ as ordinate and S as abscissa. From known expressions, worked out by Verwey and Overbeek (*loc. cit.*) for the energy of repulsion V_R and the energy of attraction V_A, an evaluation of V_m was made and this led to the equation :

$$\log W = -(\varkappa + \tfrac{1}{2})\log cz^2 - (2\varkappa + \tfrac{1}{2})\log \frac{4.9 \times 10^4 z^2 A}{\gamma^2} - (\varkappa + \tfrac{1}{2})\log \frac{8\pi e^2 N \times 10^{-6}}{DkT} - \log 2a \qquad \ldots (5)$$

where $$\varkappa = \frac{0.85 \times 10^{-6} a\gamma^2}{kTz^2}, \qquad \gamma = \frac{\exp\left(\frac{ze\,\psi_0}{2\,kT}\right) - 1}{\exp\left(\frac{ze\,\psi_0}{2\,kT}\right) + 1}$$

z represents valency, A, the van der Waals attraction constant, e, the electronic charge, N, the Avogadro number, D, the dielectric constant, $k = R/N$ and T, the temperature and ψ_0, the surface potential of the colloidal particles.

For a given colloid and electrolyte, assuming all the terms excepting c as constants, equation (5) can be expressed as follows :

$$\log W = -(\varkappa + \tfrac{1}{2})\log c - \log K \qquad \ldots (6)$$

where K stands for all the constant terms. Therefore, a plot of log W against - log c

will yield a straight line. This relationship has been confirmed by Reerink from his own data on silver iodide sol and those of others on a few colloids.

Since Reerink's equation has got a theoretical basis, it is worthwhile considering if Bhattacharya's equation can be deduced from it. How this can be done is discussed below.

Equation (6) can be expressed as

$$W = \frac{1}{Kc^{\beta}} , \qquad \ldots \quad (7)$$

where $\beta = (\alpha + \frac{1}{2}) > 1$.

Writing $c = a_1 + (c - a_1)$, where a_1 is a constant and less than c, equation (6) may be put in the form :

$$W = \frac{1}{K\left\{ a_1 + (c - a_1) \right\}^{\beta}} = \frac{1}{Ka_1{}^{\beta} \left\{ 1 + \left(\frac{c - a_1}{a_1} \right) \right\}^{\beta}}$$

$$= \frac{1}{Ka_1{}^{\beta} \left\{ 1 + \frac{\beta(c - a_1)}{a_1} \right\}} .$$

Since terms involving higher powers of $(c - a_1)/a_1$ can be neglected by adjusting the values of c in such a way that $\beta(c - a_1)/a_1$ is always a fraction. Under this condition we have

$$W = \frac{1}{Ka_1{}^{\beta-1} \beta \left\{ c - \frac{a_1(\beta - 1)}{\beta} \right\}}$$

$$= \frac{1}{Ka_1{}^{\beta-1} (c - a)\beta} \qquad \ldots \quad (8)$$

where $a = \frac{a_1 (\beta - 1)}{\beta}$ = a constant.

Now, $W = t/T$ where t is the time required for coagulation when the concentration of the added electrolyte is c, and T is the time required at a sufficiently high concentration of an electrolyte when the velocity of coagulation is the most rapid and constant.

According to Smoluchowski's equation for rapid coagulation

$$T = \frac{1}{8\pi D a n_0} .$$

As the stability ratio W cannot be less than unity, we may also write $W = (t + T)/T$ so that even if t be put equal to zero, W cannot be less than unity. Using this expression for W, equation (8) can be written as

$$\frac{t}{T} + 1 = \frac{1}{Ka_1{}^{\beta-1}(c - a)\beta}$$

or $\frac{nt}{m} + \frac{1}{m} = \frac{1}{c - a}$ $\qquad \ldots \qquad \ldots \quad (9)$

where $Ka_1{}^{\beta-1} . \beta = \frac{1}{m}$ and $\frac{1}{T} = n$.

It will be noticed that equation (9) is identical in form with that of Bhattacharya *et al.* (*loc. cit.*).

The point that remains to be decided is the extent to which c may be allowed to vary with respect to a_1, and therefore, to a. Suppose for a given time t of coagulation, experimental error in determining c is of the order of 5%. Then we may neglect $\beta(\beta-1)\{(c-a_1)/a_1\}^2$ that is the third term in the expansion of

$$\left\{1+\left(\frac{c-a_1}{a_1}\right)\right\}^{\beta}$$

provided that

$$\beta(\beta-1)(c-a_1)^2=0.05\left\{1+\beta\left(\frac{c-a_1}{a_1}\right)\right\} \quad \ldots (10)$$

An approximate solution of equation (10) gives

$$c=a_1\left(1+\frac{0.35}{\beta-1}\right)=a\left(\frac{\beta}{\beta-1}\right)\left(1+\frac{0.35}{\beta-1}\right) \quad \ldots (11)$$

If β be put equal to 5, 4 and 3 respectively, then from equation (11) the corresponding values of c are found to be a (1.25×1.09), a (1.33×1.12), a (1.5×1.18). The limiting value of c with respect to a thus increases as β decreases. The experimental results indicate that when c is varied within the prescribed limit, t usually varies over a wide range. Thus, a justification of Bhattacharya's equation can be found on theoretical grounds.

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STUDIES IN POLYCYCLIC SYSTEMS. PART V*. SYNTHESIS OF METHYLPICENES

By D. Nasipuri and J. Roy

A few extensions of the synthesis of picene (Nasipuri, *J. Chem. Soc.*, 1958, 2618) have been studied with the result that a flexible new route to methylpicenes is made available which has been used here for the synthesis of a number of mono- and polymethylpicenes, viz., 1-methyl-, 1:2-dimethyl-, 2:3-dimethyl-, 2:5-dimethyl-, 1:5-dimethyl- and 1:2:5-trimethyl-picenes, all of which are unknown.

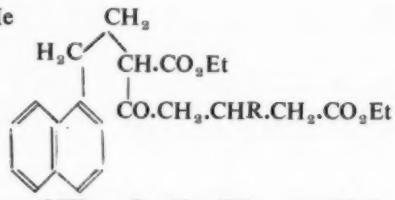
In an earlier communication (Nasipuri, *J. Chem. Soc.*, 1958, 2618), a new synthesis of picene by the Robinson ring-extension (du Feu, McQuillin and Robinson, *ibid.*, 1937, 53) of 2-alkoxycarbonyl-1:2:3:4-tetrahydro-1-oxochrysene (e.g., V) was described. Several possible extensions of this synthesis have now been investigated. Three main variations have been studied in this connection, viz., (A) the use of β-chloroketones such as 1-chloropentan-3-one (II) as alkylating agent in place of the methiodide of the Mannich-base leading to the synthesis of 1-methylpicenes, (B) the use of the Mannich-base other than that of acetone, e.g., butan-2-one, and (C) the use of ethyl 2 - methyl - 4:6 - dioxoheptane - 1:5 - dicarboxylate(Ib) in place of ethyl 4:6-dioxoheptane-1:5-dicarboxylate(Ia) in the original synthesis, leading to the preparation of 5-methylpicenes. By a suitable combination of these variations, a general method for the synthesis of substituted picenes, capable of very wide and varied application, has thus been developed. Methylpicenes, it may be pointed out, are important in connection with the structural investigations of many triterpenoids (Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, **15**, 431, 1496; 1932, **15**, 1285; 1937, **20**, 791; *Annalen*, 1927, **471**, 21; Noller, *J. Amer. Chem. Soc.*, 1934, **56**, 1582; Drake and Duvall, *ibid.*, 1936, **58**, 1684; Wieland *et al.*, *Annalen*, 1936, **522**, 191; Spring and Vickerstaff, *J. Chem. Soc.*, 1937, 249; Simpson and Williams, *ibid.*, 1938, 686; Miesels *et al.*, *Helv. Chim. Acta*, 1949, **32**, 1075; 1955, **38**, 1298; Newman and Cline, *J. Org. Chem.*, 1951, **16**, 934; Nasipuri, *J. Chem. Soc.*, 1958, 4192). The following is an account of the synthetical operations.

In route A, 1-chloropentan-3-one (II) was used for alkylating 1:2:3:4-tetrahydro-2-methoxycarbonyl-1-oxochrysene (Va). The latter was prepared from ethyl α-(2-1′-naphthylethyl)- β -oxopimelate (IIIa) by essentially the same steps as described by Nasipuri (*loc. cit.*). An attempt to increase the yield at the cyclodehydration stage by using polyphosphoric acid (Koo, *J. Amer. Chem. Soc.*, 1953, **75**, 720, 1889, 2000; Koo and Hartwell, *ibid.*, 1953, **75**, 1625) failed. However, by lowering the temperature of sulphuric acid to -20° and using a little ether as co-solvent, the yield was considerably increased and the product on hydrolysis afforded the unsaturated acid (IVa) in 55-60% yield. The dimethyl ester of the latter was dehydrogenated with sulphur and then submitted to the Dieckmann cyclisation. The resultant sodio derivative of the β-oxo-ester (Va) was treated *in situ* with 1-chloropentan-3-

* Part IV, *J. Chem. Soc.*, 1958, 4192.

$EtO_2C.CH_2.CHR.CH_2.CO.CH(CO_2Et).COMe$

[Ia : R=H; Ib : R=Me]



[IIIa : R=H; IIIb : R=Me]

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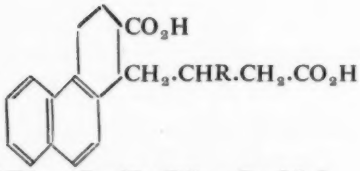
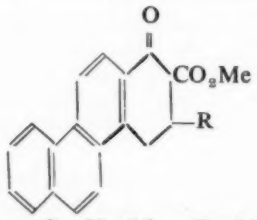
(II)

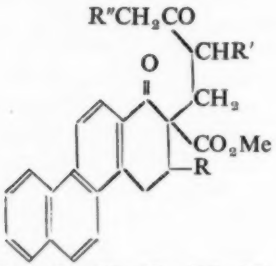


[IVa : R=H; IVb : R=Me]

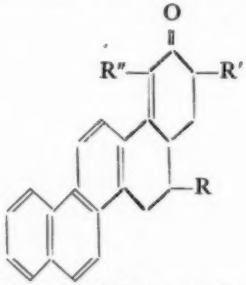


[Va : R=H; Vb : R=Me]

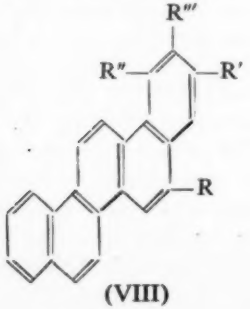
-one (II), prepared according to McMahon *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 2971). The dioxo-ester (VIa), m.p. 160-61°, was isolated from the reaction mixture in nearly 75% yield and cyclised to 2:3:4:4a:5:6-hexahydro-1-methyl-2-oxopicene (VIIa) by refluxing hydrochloric acid and acetic acid (Wilds and Shunk,



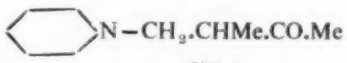
[VIa : R=R′=H; R″=Me.
VIb : R=R″=H; R′=Me.
VIc : R′=R″=H; R=Me
VId : R′=H; R=R″=Me]



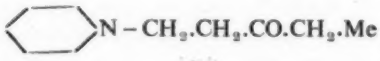
[VIIa : R=R′=H; R″=Me
VIIb : R=R″=H; R′=Me
VIIc : R′=R″=H; R=Me
VIId : R′=H; R=R″=Me]



(VIII)



(IX)



(X)

J. Amer. Chem. Soc., 1943, **65**, 469; Wilds and Close, *ibid.*, 1946, **68**, 83; Wilds and Werth, *J. Org. Chem.*, 1952, **17**, 1149). The ketone (VIIa) was then reduced with lithium aluminium hydride and the resultant alcohol dehydrated and dehydrogenated by heating with 30% palladium-charcoal (Linstead and Thomas, *J. Chem. Soc.*, 1940, 1127) to furnish 1-methylpicene (VIII : R=R′=R‴=H; R″=Me), m.p. 213°, in excellent yield. Treatment of the ketone (VIIa) with an excess of methylmagnesium iodide, followed by dehydration and dehydrogenation of the resultant alcohol, afforded 1:2-dimethylpicene (VIII : R=R′=H; R″=R‴=Me), m.p. 228°. Both the picenes afforded red 2:4:7-trinitrofluorenone complex (Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727).

In route B, the methiodide of 3-methyl-4-piperidinobutan-2-one (IX) (Mannich and Hof, *Arch. Pharm.*, 1927, **265**, 489) was condensed with the potassio derivative of the β-oxo-ester (Va) and the corresponding dioxo-ester (VIb), m.p. 133°, was obtained in somewhat poor yield (40-45%). During the formation of 3-methyl-4-piperidinobutan-2-one (IX), the isomeric 5-piperidinopentan-3-one (X) was likely to be present as a contaminant (*loc. cit.*). It has been proved, however, that the former is always the major product (Downes *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 3465), and in case the latter was produced in any appreciable amount, the condensation with β-oxo-ester (Va) would lead to the formation of the isomeric dioxo-ester (VIa), m.p. 160-61°. The two compounds gave mixed melting point much lower than either of the two. The homogeneity of the product (VIb) was thus assured. Hydrolysis and cyclisation of the dioxo-ester by refluxing with acetic acid and hydrochloric acid afforded 2:3:4:4a:5:6-hexahydro-3-methyl-2-oxopicene (VIIb). The latter was then converted into 2:3-dimethylpicene (VIII : R=R″=H; R′=R‴=Me), m.p. 229° (2:4:7-trinitrofluorenone complex, m.p. 222.5°) by treatment with methylmagnesium iodide, followed by simultaneous dehydration and dehydrogenation as before.

In the third variation of the method, 2-1′-naphthylethyl bromide was condensed with ethyl 2-methyl-4:6-dioxoheptane-1:5-dicarboxylate (Ib) (Adhya *et al.*, *J. Chem. Soc.*, 1956, 1346) according to Bouveault and Bongart (*Bull. soc. chim.*, 1902, **27**, 1100) to afford the β-oxo-ester (IIIb) in good yield. The latter was cyclodehydrated as before by concentrated sulphuric acid at 0° to the unsaturated acid (IVb). The corresponding dimethyl ester on dehydrogenation and the Dieckmann condensation gave 1:2:3:4-tetrahydro-2-methoxycarbonyl-3-methyl-1-oxochrysene (Vb), the sodio derivative of which was treated with the methiodide of 4-piperidinobutan-2-one (Wilds and Werth, *loc. cit.*). The product was worked up in the usual way to furnish 1:2:3:4-tetrahydro-2-methoxycarbonyl-3-methyl-1-oxo-2:3′-oxobutylchrysene (VIc), m.p. 142-44° in 58-68% yield. This was heated with refluxing hydrochloric acid and acetic acid and the resultant picene-ketone (VIIc), m.p. 252-53°, was converted into 2:5-dimethylpicene (VIII: R=R‴=Me; R′=R″=H), m.p. 263° (trinitrofluorenone complex, m.p. 284-85°).

Finally, the sodio derivative of the β-oxo-ester (Vb) was condensed with 1-chloropentan-3-one (II) and the dioxo-ester (VId), m.p. 126-27°, isolated in good yield. This in turn was cyclised to the pentacyclic ketone (VIId), m.p. 207°, and the latter converted into 1:5-dimethylpicene (VIII : R‴=R′=H; R″=R=Me), m.p. 195-97° and 1 : 2 : 5-trimethylpicene (VIII : R′=H; R=R″=R‴=Me), m.p.

199-200° (trinitrofluorenone complex, m.p. 240-42° and 239-40° respectively) by methods already described.

The ultraviolet absorption spectra of these methylpicenes compared favourably with those of picene (Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235).

EXPERIMENTAL*

Route A : Synthesis of 1-Methylpicenes

Ethyl (2-1′-Naphthylethyl)-β-oxopimelate (IIIa).—The following method of preparation was found to be more satisfactory than that described in the original synthesis (*loc. cit.*) : To a solution of potassium (8.8 g.) in butanol[r] (175 c.c.) was added ethyl 2-oxopentane-1:5-dicarboxylate (49 g.) (Nasipuri and Guha, unpublished work; Hunter and Hogg, *J. Amer. Chem. Soc.*, 1949, **71**, 1924). Then 2-1′-naphthylethyl bromide (56 g.) was rapidly added and the mixture heated under reflux for 20 hours in an atmosphere of nitrogen. After removal of most of the butanol at the water-pump, the residue was made acidic with cold 2*N*-H_2SO_4 and the heavy organic layer was taken up in ether. The ethereal solution was washed with water, dried and the solvent evaporated. The product was distilled carefully in an oil-bath up to 150° at 0.2 mm in order to eliminate low-boiling impurities as far as possible, and the residue (70 g.) was used for the next operation.

γ-(2-Carboxy-3:4-dihydro-1-phenanthryl)-butyric Acid (IVa).—(*a*). The above condensation product (6 g.) in dry ether (6 c.c.) was treated with H_2SO_4 (conc., 20 c.c.) in a bath of dry ice in acetone at -20° for 30 mins. The product, worked up in the usual way, on hydrolysis afforded the acid (IVa, 3.2 g.), m.p. 203°. (Found : C, 73.7; H, 5.8. Calc. for $C_{19}H_{18}O_4$: C, 73.5 ; H, 5.8%).

(*b*). In an attempt to effect the cyclodehydration by polyphosphoric acid, the condensation product (IIIa, 2 g.) was stirred in polyphosphoric acid (from P_2O_5, 11g. and 89% orthophosphoric acid 9 c.c.), for 1 hour at room temperature. The mixture was cooled, diluted with ice-water and extracted thoroughly with ether. The residue after evaporation of the ether was hydrolysed with 10% EtOH—KOH; a gummy acid was obtained which crystallised from acetic acid to furnish (IVa), m.p. 200-20°, in very poor yield (*ca.* 10%).

1:2:3:4 - *Tetrahydro - 2 - methoxycarbonyl - 1 - oxo - 2 - 3′ - oxopentylchrysene* (VIa).—The dimethyl ester of the preceding acid was dehydrogenated with 1 g. atom of sulphur and the corresponding aromatic ester (3.4 g.), m.p. 72-73°, was heated with a suspension of finely divided sodium (0.3 g.) in benzene (20 c.c.), containing a few drops of methanol. When the formation of sodio-salt of the β-oxo-ester (Va) was complete (2-3 hrs.), the flask was cooled in an ice-bath and 1-chloropentan-3-one (II), b.p. 55-57°|8 mm (3 g.), in dry benzene (10 c.c.) added with shaking. After 1 hour the flask was taken out of ice and left at room temperature

* All melting and boiling points are uncorrected. The ultraviolet absorption spectra were recorded on Unicum spectrophotometer.

overnight. Next day, the almost clear solution was heated on the water-bath for 1 hour, cooled and diluted with ice-water containing H_2SO_4 (1 c.c.). The product was extracted with benzene and the benzene layer was washed successively with dilute acid, sodium carbonate solution and water. After removal of the benzene, the residual solid was crystallised from ethyl acetate to furnish (VIa) (2.6 g), m.p. 160-61°. (Found : C, 76.8 ; H, 6.1. $C_{25}H_{24}O_4$ requires C, 77.3 ; H, 6.2%).

2:3:4:4a:5:6-*Hexahydro*-1-*methyl*-2-*oxopicene* (VIIa).—The above dioxo-ester (VIa) (2.6 g.) was refluxed with glacial acetic acid (50 c.c.), HCl (conc., 25 c.c.) and water (5 c.c.) for 20 hours under CO_2 atmosphere. The solution was cooled, diluted with water and the solid (2.2 g.), m.p. 190-210°, was collected by filtration. After a few crystallisations from benzene (charcoal), (VIIa) melted at 233°. (Found : C, 88.7 ; H, 6.6. $C_{23}H_{20}O$ requires C, 88.5 ; H, 6.4%).

1-*Methylpicene*.—A solution of the foregoing ketone (0.3 g.) in tetrahydrofuran (15 c.c.) was added to $LiAlH_4$ (0.3 g.), suspended in ether (10 c.c.). The reaction mixture was gently refluxed for 2 hours, cooled and decomposed with ethanol and dilute sulphuric acid. The residue (0.3 g.) on evaporation of the solvent was heated with 30% palladium-charcoal (70 mg.) at 340° for 1 hour and sublimed in high *vacuo* to afford 1-methylpicene (0.18 g.) which crystallised from benzene in fluorescent plates, m.p. 213° ; $\lambda_{max.}$ (in $CHCl_3$) 259, 279, 288, 320, 334, 363 and 381 mμ (log ε 4.70, 4.88, 5.04, 4.29, 4.36, 3.03 and 2.96 respectively) ; $\lambda_{min.}$ 264, 315, 327, 357 and 375 mμ (log ε 4.66, 4.28, 4.18, 2.9 and 2.71 respectively). (Found : C, 94.3 ; H, 5.5. $C_{23}H_{16}$ requires C, 94.5 ; H, 5.5%).

The 2:4:7-*trinitrofluorenone complex*, prepared in benzene-alcohol mixture, was crystallised from glacial acetic acid in red needles, m.p. 234-35°. (Found : C, 71.0 ; H, 3.4 ; N, 6.9. $C_{23}H_{16}$,$C_{13}H_5O_7N_3$ requires C, 71.2 ; H, 3.5 ; N, 6.9%).

1:2-*Dimethylpicene*.—A solution of the ketone (VIIa) (0.3 g.) in dry benzene (30 c.c.) was treated with an excess of MeMgI (from magnesium 0.3 g. and MeI 0.9 c.c.) in dry ether (20 c.c.). The resultant alcohol (0.3 g.) was heated with 30% palladium-charcoal (70 mg.) at 340° for 1 hour and the product on sublimation in high *vacuo* and crystallisation from benzene furnished 1:2-*dimethylpicene* (150 mg.), m.p. 227-28° ; $\lambda_{max.}$ (in $CHCl_3$) 260, 290, 323, 338, 366 and 385 mμ (log ε 4.67, 4.96, 4.25, 4.29, 3.03 and 2.93 respectively) ; $\lambda_{min.}$ 265, 318, 330, 360 and 375 mμ (log ε 4.63, 4.20, 4.18, 2.98 and 2.77 respectively). (Found : C, 93.9 ; H, 5.8. $C_{24}H_{18}$ requires C,94.1 ; H,5.9%).

The 2:4:7-*trinitrofluorenone complex*, prepared in benzene-ethanol mixture, was crystallised from acetic acid in red needles, m.p. 225°. (Found : C, 71.5 ; H, 3.6 ; N, 6.6. $C_{24}H_{18}$, $C_{13}H_5O_7N_3$ requires C, 71.5 ; H, 3.7 ; N, 6.7%).

Route B : Synthesis of 3-*Methylpicenes*

1:2:3:4 - *Tetrahydro* - 2 - *methoxycarbonyl* - 2 - (2′ - *methyl* - 3′ - *oxobutyl*)-1-*oxochrysene* (VIb).—To a cooled suspension of the potassio derivative of the β-oxo-ester (Va), prepared by heating methyl γ-(2-methoxycarbonyl-1-phenanthryl)-butyrate (7.5 g.) and pulverised potassium (1.15 g.) in dry benzene (30 c.c.),

was added a solution of the methiodide of 3-methyl-4-piperidinobutan-2-one (from 9 g. of the Mannich base) in absolute methanol (30 c.c.). The solid disappeared after a few minutes' shaking and the solution was left overnight at room temperature. Next day, the reaction was completed by refluxing the mixture on the steam-bath for 1 hour. After cooling, the solution was diluted with acidulated water and the precipitate was extracted with benzene. The benzene extract was washed successively with water, dilute alkali, dilute acid and water. After evaporation of the solvent, the residual solid was purified through chromatography on alumina column and after a few crystallisations from ethyl acetate, the desired product (VIb) was obtained in the pure form (4.9 g.), m.p. 133°. (Found : C, 77.1 ; H, 6.0. $C_{25}H_{24}O_4$ requires C, 77.3 ; H, 6.2%).

2:3:4:4a:5:6-*Hexahydro-3-methyl-2-oxopicene* (VIIb).—The above dioxo-ester (VIb, 4 g.) was refluxed with glacial acetic acid (100 c.c.), HCl (conc., 50 c.c.) and water (10 c.c.) under CO_2 atmosphere for 15 hrs. The mixture on being diluted with water and filtered afforded (VIIb) (3 g.), m.p. 210-15°. Further crystallisations from ethyl acetate furnished colorless crystals, m.p. 225°. (Found : C, 88.6 ; H, 6.2. $C_{23}H_{20}O$ requires C, 88.5 ; H, 6.4%).

2:3-*Dimethylpicene*.—A solution of the above ketone (0.3 g.) in dry benzene (30 c.c.) was treated with an excess of MeMgI in ether, and the resultant alcohol was heated with 30% Pd-C (80 mg.) at 340° for 1 hour. The product on sublimitation and crystallisation from benzene yielded 2:3-*dimethylpicene* (120 mg.), m.p. 229° ; $\lambda_{max.}$ (in $CHCl_3$) 260, 283, 290, 324, 338, 365 and 385 mμ (log ε 4.71, 4.87, 5.0, 4.29, 4.34, 3.1 and 3.03 respectively) ; $\lambda_{min.}$ 265, 320 330, 360 and 376 mμ (log ε 4.66, 4.28, 4.22, 3.06 and 2.87 respectively). (Found : C, 94.0 ; H, 5.6. $C_{24}H_{18}$ requires C,94.1 ; H, 5.9%).

The 2:4:7-*trinitrofluorenone complex* crystallised (glacial acetic acid) in red needles, m.p. 222.5°. (Found : C, 71.3 ; H, 3.6 ; N, 6.8. $C_{24}H_{18},C_{13}H_5O_7N_3$ requires C, 71.5 ; H, 3.7 ; N, 6.7%).

Route C : Synthesis of 5-Methylpicenes

γ-(2-*Oxycarbonyl*-3:4-*dihydro* - 1 - *phenanthryl*) - β - *methylbutyric Acid* (IVb).—Ethyl 2-methyl-4:6-dioxoheptane-1:5-dicarboxylate (Ib), required in these experiments, was prepared according to Adhya *et al.* (*loc. cit.*). The ester (28.6 g.) was added slowly to an ice-cold solution of sodium ethoxide (from sodium 2.3 g. and absolute ethanol 40 c.c.) and left overnight. Next day, 2-1′-naphthylethyl bromide (23.5 g.) was added and the mixture heated at 90-92° for 15 hrs. The product, isolated in the usual way, was heated up to 150°|0.2 mm to remove most of the low-boiling fraction, and the residue (30 g.) was cyclised as follows :

The condensation product (IIIb, 5 g.) was added to H_2SO_4 (conc., 10 c.c.), cooled in a freezing mixture and stirred for 30 mins. The dark brown solution was mixed with powdered ice and the product after working up as usual was hydrolysed by 5% EtOH—KOH to (IVb) (1.5 g., 30%), which was crystallised from aqueous methanol in thick prisms, m.p. 201°. (Found : C, 74.3 ; H, 6.1. $C_{20}H_{20}O_4$ requires C, 74.1 ; H, 6.2%).

The *dimethyl ester*, prepared by refluxing the acid with a mixture of methanol (60 c.c.) and H_2SO_4 (conc., 3 c.c.), was obtained as a viscous oil, b.p. 215-20°|0.3 mm.

Methyl γ-(2-Methoxycarbonyl-1-phenanthryl)-β-methylbutyrate.—The above ester (7 g.) was heated with sulphur (0.64 g.) in a nitre-nitrate bath at 245-50° for 2hrs. The dark brown product was taken up in ethanol and hydrolysed with KOH in the usual way. The alkaline solution on acidification yielded *γ-(2-carboxy-1-phenanthryl)-β-methylbutyric acid* (6.1 g.). The *dimethyl ester*, prepared with methanolic sulphuric acid, distilled at 230-35°|3 mm and it was crystallised from methanol in needless, m.p. 95-96°. (Found : C, 75.5 ; H, 6.5. $C_{22}H_{22}O_4$ requires C, 75.4 ; H, 6.3%).

1:2:3:4 - *Tetrahydro* - 2 - *methoxycarbonyl* - 3 - *methyl* - 1 - *oxo* - 2 - 3′ - *oxobutylchrysene* (VIc).—A mixture of the preceding ester (2.3 g.), pulverised sodium (0.18 g.) and dry benzene (30 c.c.) was refluxed on the water-bath until the formation of the sodio derivative was complete. To the cooled reaction mixture was added a solution of the methiodide of 4-piperidinobutan-2-one (2.5 g.) in methanol (15 c.c.). The mixture was kept overnight and then heated under reflux for 1 hour and the product worked up as described in a similar case before to yield (VIc) (1.6 g.) which was crystallised from ethyl acetate in nodules, m.p. 142-44°. (Found : C, 84.0 ; H, 6.9. $C_{25}H_{24}O_2$ requires C, 84.2 ; H, 6.8%).

2:3:4:4a:5:6-*Hexahydro-5-methyl-2-oxopicene* (VIIc).—The above dioxo-ester (1.4 g.) was hydrolysed with refluxing acetic acid (28 c.c.), HCl (conc., 14 c.c.) and water (3 c.c.) in CO_2 atmosphere for 15 hrs. The product on working up as usual furnished (VIIc) (1.1 g.), m.p. 245-50°. Further crystallisation from benzene afforded colorless plates, m.p. 252-53°. (Found : C, 88.9 ; H, 6.2. $C_{23}H_{19}O$ requires C, 88.7 ; H, 6.2%).

2:5-*Dimethylpicene.*—A solution of the above ketone (0.3 g.) in dry benzene was treated with an excess of MeMgI in ether and the resultant crude alcohol was heated with 10% Pd-C (150 mg.) at 340° for 1 hr. The product on sublimation and crystallisation from benzene afforded 2:5-*dimethylpicene* (140 mg.), m.p. 263° ; $\lambda_{max.}$ ($CHCl_3$) 290, 325, 335, 363 and 384 mμ (log ε 4.94, 4.29, 4.24, 3.35 and 3.21 respectively) ; $\lambda_{min.}$ 268, 320, 332, 360 and 375 mμ (log ε 4.8, 4.5, 4.5, 3.3 and 3.0 respectively). (Found : C, 94.2 ; H, 5.7. $C_{24}H_{18}$ requires C, 94.1 ; H, 5.9%).

The 2:4:7-*trinitrofluorenone complex* was crystallised from acetic acid in red amorphous powder, m.p. 284-85°. (Found : C, 71.4 ; H, 3.5 ; N, 6.8. $C_{24}H_{18}$, $C_{13}H_5O_7N_3$ requires C, 71.5 ; H, 3.7 ; N, 6.7%).

1:2:3:4-*Tetrahydro* - 2 - *methoxycarbonyl* - 3 - *methyl* - 1 - *oxo* - 2 - 3′ - *-oxopentylchrysene* (VId).—To the cooled sodio derivative of (Vb, 2.3 g.) (*vide infra*) was added 1-chloropentan-3-one (II) (2 g.) in dry benzene (10 c.c.). After 1 hour, the flask was taken out of the ice-bath and left overnight at room temperature. The mixture was then refluxed for 1 hour and worked up in the usual way to afford (VId) (1.5 g.), m.p. 110-15°. On crystallisation from ethyl acetate, it melted at 126-27°. (Found : C, 77.3 ; H, 6.4. $C_{26}H_{26}O_4$ requires C, 77.6 ; H, 6.5%).

2:3:4:4a:5:6-*Hexahydro*-1:5-*dimethyl*-2-*oxopicene* (VIId).—The above dioxo-ester (VId, 1.4 g.) was hydrolysed as before to yield (VIId) which crystallised from benzene in flakes (1.0 g.), m.p. 207°. (Found : C, 88.1 ; H, 6.7. $C_{24}H_{22}O$ requires C, 88.3 ; H, 6.8%).

1:5-*Dimethylpicene*.—A solution of the preceding ketone (0.3 g.) in tetrahydrofuran (15 c.c.) was added to a suspension of $LiAlH_4$ (0.3 g.) in ether (10 c.c.) and the mixture was gently refluxed for 2 hrs. The resultant alcohol, m.p. 155-57°, was heated with 10% Pd-C (140 mg.) at 340° for 1 hour and on sublimation and crystallisation from benzene furnished 1:5-*dimethylpicene* (160 mg.) in clusters of flakes, m.p. 195-97° ; $\lambda_{max.}$ (in $CHCl_3$) 261, 290, 322, 337, 365 and 384 mμ (log ε 4.84, 4.99, 4.3, 4.34, 3.05, 2.98 respectively) ; $\lambda_{min.}$ 266, 317, 330, 360 and 375 mμ (log ε 4.6 4.26, 4.2, 2.98 and 2.78 respectively). (Found : C, 93.9 ; H, 5.8. $C_{24}H_{18}$ requires C, 94.1 ; H, 5.9%).

The 2:4:7-*trinitrofluorenone complex* formed red amorphous powder from acetic acid and had m.p. 240-42°. (Found : C, 71.3 ; H, 3.9 ; N, 6.9. $C_{24}H_{18}$, $C_{13}H_5O_7N_3$ requires C, 71.5 ; H, 3.7 ; N, 6.8%).

1:2:5-*Trimethylpicene*.—A solution of (VIId, 0.3 g.) in dry benzene was added to ethereal solution of MeMgI (excess) and the resultant alcohol, m.p. 243-45°, was dehydrated and dehydrogenated as before with 10% Pd-C (150 mg.). The product on sublimation and crystallisation from benzene afforded 1:2:5-*trimethylpicene* in cluster of plates (140 mg.), m.p. 199-200° ; $\lambda_{max.}$ (in $CHCl_3$) 258, 291, 324, 338, 365, and 385 mμ (log ε 4.67, 4.97, 4.25, 4.28, 3.03, and 2.90 respectively) ; $\lambda_{min.}$ 265, 312, 332, 360 and 376 mμ (log ε 4.6, 4.2, 4.18, 3.02 and 2.8 respectively). (Found : C, 93.5 ; H, 6.2. $C_{25}H_{20}$ requires C, 93.7 ; H, 6.3%).

The 2:4:7-*trinitrofluorenone complex*, prepared in the usual way, was crystallised from acetic acid in dark red amorphous powder, m.p. 239-40°. (Found : C, 71.7 ; H, 4.1 ; N, 6.7. $C_{25}H_{20}$,$C_{13}H_5O_7N_3$ requires C, 71.8 ; H, 3.9 ; N, 6.6%).

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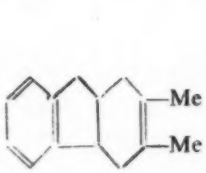
DIENE SYNTHESIS OF FLUORENE DERIVATIVES

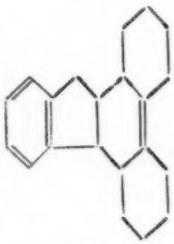
By S. C. Sengupta and Asutosh Mitra

Fluorene derivatives have been prepared from dienes which readily form adducts with indene when heated in xylene solution at 150°. The adducts, being fluorene derivatives with a carbonyl bridge, give rise to a fluorene on decarbonylation and dehydrogenation in one operation by heating with Pd-C at 300-330°.

In the literature we find only a few applications of the diene synthesis leading directly to the fluorene ring system. This ring system results when compounds of indene type function as dienophiles. Alder and Rickerd (*Ber.*, 1938, **71,** 879) had obtained a partly hydrogenated fluorene(I) when 2:3-dimethylbutadiene was heated with indene. The adduct (I) had been dehydrogenated to 2:3-dimethylfluorene. In a similar manner, a partially hydrogenated 1:2-3:4-dibenzofluorene (II) has been obtained from 1:1′-bi*cyclo*hexenyl and indene (Bergmann and Bergmann, *J. Amer. Chem. Soc.*, 1938, **60,** 1805). The adduct was converted to the parent hydrocarbon by dehydrogenation. In all these examples heating in a sealed tube at a high temperature was needed for adduct formation.



(I)

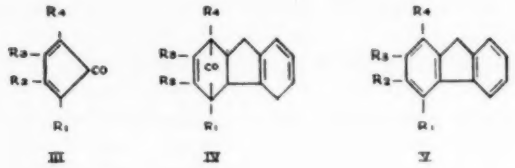


(II)

We have now found that fluorene derivatives can be prepared under less drastic conditions when reactive dienes, such as, *cyclo*pentadienone derivatives, are used. These dienes readily form adducts with indene when heated in xylene solution at about 150°. The adducts formed are fluorene derivatives with a carbonyl bridge. They could in most cases be decarbonylated and dehydrogenated to a fluorene in one operation by heating with Pd-C catalyst at 300-30°.

1:2:3:4-Tetraphenylfluorene (Va) has been synthesised starting from tetraphenyl*cyclo*pentadienone (tetracyclone) (IIIa) and indene. The adduct (IVa) is readily formed and the latter on heating with 10% Pd-C at 300° looses the carbonyl bridge and is dehydrogenated to 1:2:3:4 - tetraphenylfluorene (Va). In a similar manner 1:4-dimethyl-2:3-diphenylfluorene (Vb) has been obtained starting from 2:5-dimethyl-3:4-diphenyl*cyclo*pentadienone (IIIb) and indene.

2-Methyl-5-ethyl-3:4-diphenyl*cyclo*pentadienone (IIIc) also formed with indene a crystalline adduct (IVc), but the latter decomposed in an attempt to dehydrogenate it.



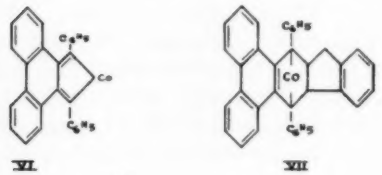
III IV V

a: $R_1 = R_2 = R_3 = R_4 = C_6H_5$

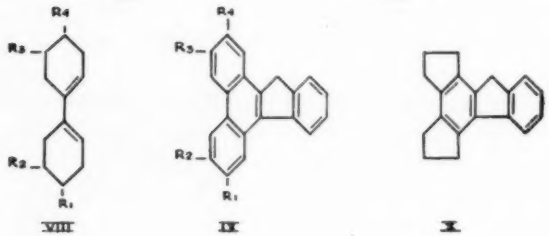
b: $R_1 = R_4 = Me$, $R_2 = R_3 = C_6H_5$

c: $R_1 = Me$, $R_2 = R_3 = C_6H_5$, $R_4 = Et$.

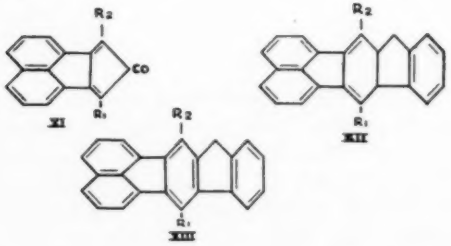
d: $R_1 = R_4 = C_6H_5$, $R_2 = R_3 = CH_2$ (O, O) C_6H_5



VI VII



VIII IX X



XI XII XIII

Piperylcyclone (IIId) and phenecyclone (VI) also readily formed adducts (IVd) and (VII) respectively with indene. The endocarbonyl bridge of the last two adducts could not be eliminated during the attempted dehydrogenation with Pd-C.

Two dibenzofluorene derivatives, namely, 1: 2-3: 4-*bis*-(2′-methylbenzo)-fluorene (IX: $R_1 = R_4 = Me$; $R_2 = R_3 = H$) and 1: 2-3: 4-*bis*-(3′-methylbenzo)-fluorene (IX: $R_1 = R_4 = H$; $R_2 = R_3 = Me$) have also been synthesised by this method. 4:4′-

Dimethyl-1 : 1′-bi*cyclo*hexenyl (VIII : $R_1 = R_4 = Me$; $R_2 = R_3 = H$) reacts with indene giving rise to the adduct which has not been obtained in a chemically pure condition, but on dehydrogenation this crude adduct affords the pure hydrocarbon 1 : 2-3 : 4-*bis*-(2′-methylbenzo)-fluorene (IX: $R_1 = R_4 = Me$; $R_2 = R_3 = H$). In a similar manner 1:2-3:4-*bis*-(3′-methylbenzo)-fluorene (IX: $R_1 = R_4 = H$; $R_2 = R_3 = Me$) has been obtained in a pure condition, starting from 5:5′-dimethyl-1:1′-bi*cyclo*hexenyl (VIII: $R_1 = R_4 = H$; $R_2 = R_3 = Me$) and indene.

This method has been extended to the synthesis of 1:2-3:4-bi*cyclo*pentenofluorene (X) starting from 1:1′-bi*cyclo*pentenyl and indene.

Two 2:3-(1′:8′-naphthylene)-fluorene derivatives (XIII) have also been synthesised. These may also be named as indeno-fluoranthenes. Acecyclone (XI: $R_1 = R_2 = Ph$) readily combines with indene forming an adduct from which the endocarbonyl bridge is eliminated at the temperature of the reaction in boiling xylene solution. The adduct (XII : $R_1 = R_2 = Ph$) on dehydrogenation furnishes 1 : 4 - diphenyl-2 : 3-(1′ : 8′ - naphthylene) - fluorene (XIII : $R_1 = R_2 = Ph$). 1:4-Dicarboxy - 10:11 - dihydro - 3 : 4 - (1′ : 8′-naphthylene) - fluorene (XII : $R_1 = R_2 = COOH$) has been obtained directly when 2:5 - diethoxycarbonyl - 3:4 - (1′:8′ - naphthylene)-*cyclo*pentadienone (XI : $R_1 = R_2 = COOEt$) is heated with indene in boiling xylene solution. The endocarbonyl group of the adduct is eliminated during the reaction. The two ethoxycarbonyl groups have also been found to be hydrolised in the course of isolation of the adduct. This compound could not be decarboxylated.

EXPERIMENTAL

1:4:10.11 - *Tetrahydro* - 1:2:3:4 - *tetraphenyl* - 1:4 - *endocarbonylfluorene* (IVa).—Tetracyclone (IIIa, 5 g.) (Dilthey and Quint, *J. parkt. Chem.*, 1930, **128,** 139) and indene (1.6 g.) in dry xylene (10 c.c.) were refluxed for 5 hours in a glycerine bath at 150° (bath temperature) and was then left overnight when the solid adduct separated. It was collected, washed with xylene and crystallised from dilute dioxan, as a white crystalline substance, m.p. 205°, yield 3.5 g. (Found : C, 91.55 ; H, 5.78. $C_{38}H_{28}O$ requires C, 91.2 ; H, 5.6%).

1:2:3:4 - *Tetraphenylfluorene* (Va).—The adduct (IVa, 2 g.) was heated with 10% Pd-C (0.2 g.) at 300° for 7 hours. The product was extracted with ether, ether removed and the solid residue was crystallised from benzene as a light yellow substance, m.p. 225-26°. (Found : C, 94.1 ; H, 5.57. $C_{37}H_{26}$ requires C, 94.46 ; H, 5.53%).

1:4:10:11 - *Tetrahydro* - 1:4 - *dimethyl* - 2:3 - *diphenyl* - 1:4 *endocarbonylfluorene* (IVb).—The dimer of 2:5 - dimethyl-3:4-diphenyl*cyclo*pentadienone (IIIb, 4.5 g.) (Gray, *J. Chem. Soc.*, 1909, **95,** 2134; Japp and Meldrum, *ibid.*, 1901, **79,** 1031) and indene (2 g.) in dry xylene (5 c.c.) were heated for 6 hours in a bath at 160°. Xylene was removed by steam distillation and the solid residue was crystallised from spirit in white crystals, m.p. 136-37°, yield 3.6 g. (Found : C, 89.7 ; H, 6.2. $C_{28}H_{24}O$ requires C, 89.3 ; H, 6.3%).

1:4 - *Dimethyl* - 2:3-*diphenylfluorene* (Vb).—The adduct (IVb, 1.5 g.) and Pd-C (0.15 g.) were heated at 250° for seven hours The product was extracted

with ether, ether removed and the residual liquid was distilled under reduced pressure. The distillate readily solidified and was crystallised from absolute alcohol, m.p. 154-55°. (Found : C, 93.64 ; H, 6.33. $C_{27}H_{22}$ requires C, 93.64 ; H, 6.35%).

1:4:10:11 - *Tetrahydro* - 1 - *methyl* - 4-*ethyl* - 2:3-*diphenyl* - 1:4-*endocarbonylfluorene* (IVc).—2 - Methyl - 5 - ethyl-3:4-diphenyl*cyclo*pentadienone (IIIc, 2 g.) (Sen Gupta and Bhattacharyya, this *Journal*, 1956, **33**, 32), indene (0.9 g.) and xylene (5 c.c.) were refluxed for 6 hours at 160° in a glycerine bath. Xylene was removed and the residual pasty mass was crystallised from spirit, m.p. 119-20°, yield 1.5 g. (Found : C, 88.9 ; H, 6.44. $C_{29}H_{26}O$ requires C, 89.23 ; H, 6.6%).

The adduct (IVc) on heating with Pd-C at 300° decomposed.

1:4:10:11 - *Tetrahydro* - 1:4 - *diphenyl* - 2:3 - bis-*dioxymethylenephenyl* - 1:4-*endocarbonylfluorene* (IVd).—Piperylcyclone (IIId, 4 g.) (Arbuzov and Akhmed-Zade, *J. Gen. Chem., U.S.S.R.*, 1942, **12**, 212) and indene (1.2 g.) in dry xylene (10 c.c.) were refluxed for four hours at 150°. On cooling solid adduct separated. This was collected, washed with xylene and crystallised from toluene as a white substance, m.p. 229-30° (decomp.), yield 3.2 g. (Found : C, 81.62; H, 5.0. $C_{40}H_{28}O_5$ requires C, 81.63 ; H, 4.76%).

The adduct (IVd) on heating with Pd-C at 300° decomposed with the formation of a tarry matter.

1:4:10:11 - *Tetrahydro* - 1:4 - *biphenyl* - 2:3 - *biphenylene* - 1:4 - *endocarbonylfluonene* (VII).—A mixture of phenecyclone (VI, 3.8 g.) and indene (1.2 g.) in xylene (20 c.c.) was refluxed for half an hour at 145° in an oil-bath when the colour of the solution was discharged. On cooling, a colorless solid separated which was crystallised from benzene, m.p. 290° (decomp.), yield 3 g. (Found : C, 91.2 ; H, 5.4. $C_{38}H_{26}O$ requires C, 91.5 ; H, 5.2%).

The adduct (VII, 2 g.) was heated with Pd-C (0.2 g.) at 300° for 4 hours and the product was extracted with benzene. After removal of the solvent the residue was crystallised from toluene, m.p. 290° (decomp.) ; mixed m.p. with the adduct (VII) remained undepressed.

Synthesis of 1:2 - 3:4 - bis-(2′-*methylbenzo*)-*fluorene* (IX: $R_1 = R_4 = Me$; $R_2 = R_3 = H$).—4 : 4′ - Dimethyl - 1 : 1′ - bi*cyclo*hexenyl (19 g.) and indene (11.6 g.) in xylene (15 c.c.) were heated at 180 - 90° for 10 hours in an oil-bath. Xylene was removed by steam distillation and the residual liquid distilled at 220°/7 mm. This adduct could not be obtained in an analytically pure condition. This crude adduct (2 g.) was heated with selenium (6 g.) for 20 hours at 320°. The product was extracted with benzene, the solvent removed and the residual liquid was distilled over sodium under reduced pressure, when the distillate readily solidified. It was crystallised from rectified spirit in colorless crystals, m.p. 120°. (Found : C, 93.48 ; H, 6.4. $C_{23}H_{18}$ requires C, 93.87 ; H, 6.12%).

Synthesis of 1:2 - 3:4-bis-(3′-*methylbenzo*)-*fluorene* (IX : $R_1 = R_4 = H$; $R_2 = R_3 = Me$).—5 : 5′ - Dimethyl - 1 : 1′ -bi*cyclo*hexenyl (9 g.) was heated with indene (12 g.) for 10 hours at 180°-90° in an oil-bath. The product was distilled under reduced pressure and the fraction boiling at 210|5° mm was collected as a viscous mass. This adduct did not solidify and it was not analytically pure.

This crude adduct (2 g.) was heated with selenium (6 g.) at 320° for 20 hours. The product was extracted with ether and after removal of the solvent, the residual liquid was distilled over sodium under reduced pressure when a colorless liquid with hydrocarbon odour was obtained at 165°/5 mm. (Found : C, 93.6; H, 6.2. $C_{23}H_{18}$ requires C, 93.87 ; H, 6.12%).

Synthesis of 1:2-3:4 *bicyclopentenofluorene* (X).—1:1′-Bicyclopentenyl (13.4 g.) was refluxed with indene (20 g.) in an oil-bath at 180° for 12 hours. Unchanged indene was removed by steam distillation. The residual oil was extracted with ether, dried over calcium chloride, the solvent removed and distilled under reduced pressure. The higher fraction collected at 200-10°/5 mm was obtained as a viscous liquid. The adduct so obtained was not analytically pure. This adduct (2 g.) was heated with sulphur (4 g.) for 6 hours at 250°. The product was extracted with ether, the ether removed and the residue was distilled over sodium under reduced pressure. The distillate readily solidified. It was crystallised from alcohol, m.p. 128-29°. (Found : C, 92.54 ; H, 7.3. $C_{19}H_{18}$ requires C, 92.68 ; H, 7.31%).

1:4-*Diphenyl*-10:11-*dihydro*-2:3-(1′:8′-*naphthylene*)-*fluorene* (XII: $R_1 = R_2 = Ph$).—Acecyclone (XI : $R_1 = R_2 = C_6H_5$; 3.5 g.) (Dilthey *et al., J. prakt. Chem.*, 1935, **143,** 189) and indene (1.2 g.) in dry xylene (10 c.c.) were refluxed at 150° in a glycerine bath for 5 hours. Carbon monoxide evolved could be burnt at the mouth of the reflux condenser. The colour of the solution was slowly discharged. Xylene was removed by steam distillation and the yellow pasty residue was crystallised from benzene, m.p. 187-88°. (Found : C, 94.3; H, 5.7. $C_{35}H_{24}$ requires C, 94.59 ; H, 5.4%).

1 : 4 - *Diphenyl* - 2 : 3 - (1′ : 8′ - *naphthylene*) - *fluorene* (XIII : $R_1 = R_2 = Ph$).—The adduct (XII : $R_1 = R_2 = Ph$; 1 g.) was heated with Pd-C (0.1 g.) at 300° for 4 hours; the product was extracted with benzene from which it was crystallised, m.p. 250°. (Found : C, 95.24 ; H, 5.2. $C_{35}H_{22}$ requires C, 95.02 ; H, 4.98%).

1:4 - *Dicarboxy* - 10:11 - *dihydro*-3:4-(1′ : 8′ -*naphthylene*)-*fluorene* (XII : $R_1 = R_2 = COOH$).—2 : 5-Diethoxycarbonyl - 3 : 4 -(1′ : 8′-naphthylene)-*cyclo*pentadienone (XI : $R_1 = R_2 = COOEt$; 6.9 g.) was refluxed with indene (2.3 g.) in xylene (6 c.c.) in an oil-bath at 140° for 7 hours till the colour of the solution became very light. The solvent and excess indene were removed by steam, when a solid crystalline adduct was obtained. It was crystallised from xylene as yellow crystals, m.p. 255°, yield 3 g. (Found : C, 78.9 ; H, 3.9. $C_{25}H_{16}O_4$ requires C, 78.94 ; H, 4.21%).

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ESTIMATION OF COPPER BY α-β-DIOXIMINOACETOACETANILIDE

By J. S. Dave and A. M. Talati

α-β-Dioximinoacetoacetanilide precipitates copper quantitatively as $CuC_{20}H_{20}O_6N_6$. The gravimetric estimation of copper by this reagent and the effect of *p*H, anions and cations on this estimation have been investigated.

Dimethylglyoxime and other α-dioximes have been used as reagents for the gravimetric estimation of nickel and palladium, but none of these dioximes is known to be useful as a reagent for the gravimetric estimation of copper. It has been observed in the present investigations that α-β-dioximinoacetoacetanilide precipitates not only nickel and palladium but also copper quantitatively under definite conditions. Hence, the applicability of α-β-dioximinoacetoacetanilide as a reagent for the gravimetric estimation of copper has been undertaken. Copper forms brown chelate with this dioxime, which is represented as CuD_2, where DH is a dioxime molecule. It is quantitatively precipitated within the *p*H range of 4.4—8.3 and the estimation is not interfered by the presence of various ions under investigation.

Experimental

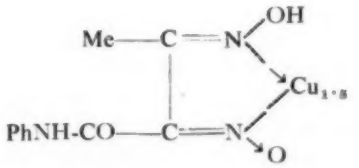
1% Alcoholic solution of α-β-dioximinoacetoacetanilide, prepared from acetoacetanilide (Dave and Talati, *Curr. Sci.*, 1957, **26**, 326), was used in all the estimations. Stock solutions of copper were prepared from AnalaR copper chloride. Copper content of this solution was determined iodometrically. Other reagents used were of C. P. grade.

Composition of the Complex.—Copper chloride solution (10 c.c.) was diluted to about 100 c.c. with distilled water and to the warm solution was added excess of the reagent solution (1 g. reagent = 0.09 g. Cu) and *p*H was adjusted to 6-7. Brown precipitates were obtained and digested on the water-bath for about an hour. The precipitates were filtered, washed with water and alcohol, and dried at 110-20°. A weighed quantity of this complex was treated with aqua regia to oxidise all organic matter and the solution was then evaporated nearly to dryness in presence of H_2SO_4. The residue was extracted with HCl (dil.) and its copper content was determined iodometrically. (Found: Cu, 12.67; 12.62. Calc. for $CuC_{20}H_{20}O_6N_6$: Cu, 12.61%).

TABLE I

Cu taken.	Salt added.		Cu chelate obtained.	Cu found.	Error.
7.85 mg.	..	..	61.9 mg.	7.81 mg.	—0.04 mg.
15.25	..	..	120.7	15.22	—0.03
23.10	..	..	182.5	23.01	—0.09
7.85	KBr,	2.0 g.	61.8	7.79	—0.06
7.85	KI,	2.0	62.0	7.82	—0.03
7.85	$NaNO_3$	2.0	62.0	7.82	—0.03
7.85	K_2SO_4	2.0	62.0	7.82	—0.03
7.85	$CaCl_2$	0.55	62.4	7.87	+0.02
7.85	$MgCl_2$	0.50	62.1	7.83	—0.02
7.85	$BaCl_2$	0.75	62.5	7.88	+0.03
7.85	$Sr(NO_3)_2$	0.65	62.15	7.84	—0.01
7.85	$CdSO_4$	0.032	61.8	7.79	—0.06

The results suggest that the composition of the precipitate can be represented as



Procedure.—An aliquot quantity of $CuCl_2$ solution was diluted to 200 c.c. with distilled water, warmed and then to it was added a sufficient amount of 1% reagent solution (1 g. reagent = 0.09 g. Cu), and *p*H was adjusted to 6-7. The precipitates were digested on a water-bath for about ½ hour, filtered, washed with water, and dried to a constant weight at 110-20°. The precipitates were weighed as $C_{20}H_{20}O_6N_6$, the factor for Cu being 0.1261. Some of the results are recorded in Table I.

Effect of *p*H.—In order to study the *p*H range over which copper can be completely precipitated by this reagent, the estimation of copper was carried out in solutions having different *p*H values. The *p*H values of the undiluted filtrates were measured with L and N *p*H meter. The *p*H range within which copper is completely precipitated by this dioxime is shown in Table II. The results indicate that copper is completely precipitated by the reagent within the *p*H range of 4.4 to 8.3.

TABLE II

*p*H ..	3.80	4.34	4.98	5.42	6.08	8.30
Cu taken (mg.)	15.25	15.25	15.25	15.25	7.85	7.85
found (mg.)	14.83	15.18	15.28	15.16	7.81	7.79

Effect of Anions and Cations.—Copper was estimated in presence of different anions and cations by the reagent at *p*H 6 to 7. The results shown in Table I indicate that bromide, iodide, nitrate, sulphate, calcium, strontium, barium, magnesium, zinc and cadmium do not interfere with the estimation of copper.

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FRIES REARRANGEMENTS OF THE ESTERS OF 4-NITRORESORCINOL

By G. C. Amin *, A. S. U. Chaughuley and G. V. Jadhav

The Fries rearrangement of 4-nitroresorcinol diacetate, dipropionate, dibutyrate, dibenzoate and the two monobenzoates furnishes 2-acyl-4-nitroresorcinols. However, the diacetate and the dipropionate afford 2:6-diacyl-4-nitroresorcinols in addition to the monoketones. The presence of the nitro group in the 4-position of the resorcinol nucleus does not hinder the Fries reaction.

In continuation of the work on the Fries rearrangement of the negatively substituted phenolic esters (this *Journal*, 1959, **36**, 617), the Fries rearrangement of the esters of 4-nitroresorcinol has been described in the present communication.

4-Nitroresorcinol diacetate (II:R=Me) rearranged to 2-acetyl-4-nitroresorcinol (III:R=Me) in absence of a solvent; however, in presence of nitrobenzene, the ester affords the same ketone along with 2:6-diacetyl-4-nitroresorcinol (IV:R=Me).

The constitution of the monoketone (II:R=Me) was confirmed by direct comparison with an authentic sample, kindly supplied by Dr. R. M. Naik (Naik, *et al.*, *Proc. Ind. Acad. Sci.*, 1953, **37A**, 765). The authentic sample of the diketone (IV : R = Me) was obtained by the nitration of 2:6-diacetylresorcinol (V:R = Me). The yields of the products are better in nitrobenzene.

Similarly, 4-nitroresorcinol dipropionate (II : R = Et) and dibutyrate (II : R = Pr^n) on the Fries isomerisation furnished 2-propionyl-(III : R = Et) and 2-butyryl (III : R = Pr^n)-4-nitroresorcinols respectively. In nitrobenzene solution, the dipropionate (II:R = Me) gave 2:6-dipropionyl-4-nitroresorcinol (IV:R = Et) which was also obtained by the nitration of 2:6-dipropionylresorcinol (V: R = Et), but in the case of the dibutyrate (II:R = Pr^n) no corresponding diketone could be obtained under several experimental conditions of the migration.

On the other hand, the rearrangement of 4-nitroresorcinol l-monobenzoate (VI) and its 3-monobenzoate (VII) either in presence or in absence of nitrobenzene provided the same product, 2-benzoyl-4-nitroresorcinol (III:R = Ph). Similarly, 4-nitroresorcinol dibenzoate (II:R = Ph) afforded also the same ketone alone. Some benzoic acid and 4-nitroresorcinol (I) were recovered on working up the reaction mixtures in case of these three benzoates. 4-Nitroresorcinol dibenzoate (II:R = Ph) could not be prepared by the direct nitration of resorcinol dibenzoate under several experimental conditions.

In order to prepare an authentic sample of 2:6-diacetyl-4-nitroresorcinol (IV:R = Me) the Fries migration of the diacetate of 5-nitroresacetophenone (m.p. 79-80°; cf. Omer and Hamilton, *J. Amer. Chem. Soc.*, 1937, **59**, 643) was attempted under several experimental conditions, but in all cases the deacetylated 5-nitroresacetophenone only could be recovered.

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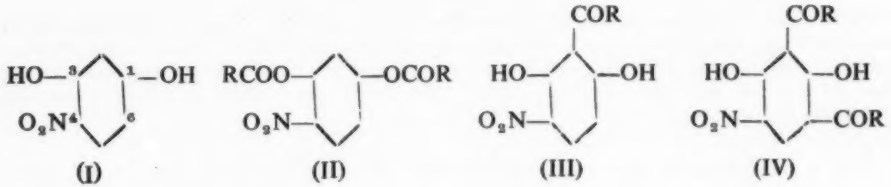
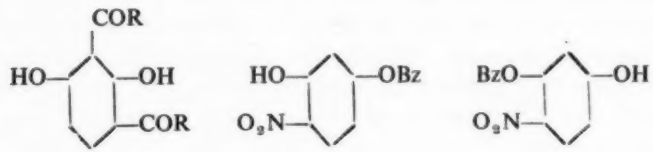
It is significant from the above results that no monoketone of the type 6-acyl-4-nitroresorcinol could be obtained in any of the esters studied above though β-or 6-position in the 4-nitroresorcinol nucleus is available for the substitution. The main products in all cases are the isomeric 2-acyl derivatives. This behaviour is parallel to the Friedel-Crafts acylations of 4-nitroresorcinol as observed by Naik *et al.* (*loc. cit.*).



(I) (II) (III) (IV)



(V) (VI) (VII)

[R = Me, Et, Pr^n, Ph.]

EXPERIMENTAL

4-Nitroresorcinol (I) was prepared by the nitration of a mixture of resorcinol, mono- and dibenzoates, followed by alkaline hydrolysis. It was crystallised from benzene in orange-red prisms, m.p. 122° (Kaufmann and Kugel, *Ber.*, 1911, **44,** 753 ; Naik *et al.*, *loc. cit.*).

Fries Rearrangement of 4-*Nitroresorcinol Diacetate*

4-Nitroresorcinol diacetate (II:R=Me) was prepared by acetic anhydride—pyridine method. It was crystallised from ethanol as slightly discoloured plates, m.p. 90°. Errera (*Gazzetta*, 1885, **15,** 273) reported the same m.p.

Formation of 2-*Acetyl*-4-*nitroresorcinol* (III:R=Me) *and* 2:6-*Diacetyl*-4-*nitroresorcinol* (IV:R=Me).—(*a*). A mixture of (II, 3 g., 1 *M*) and anhydrous aluminium chloride (8.5 g., 3.3 *M*) was heated at 140° for about 3 hours. After decomposition of the reaction mixture with ice and HCl (5 c.c.), the brown solid obtained was crystallised from ethanol in slim yellow needles, m.p. 116-17°, yield 0.7 g. It was identified as 2-acetyl-4-nitroresorcinol (III:R = Me) by direct comparison with a sample supplied by Dr. R. M. Naik. No other pure product could be isolated on working up the filtrate and other tailings.

(*b*). When nitrobenzene (45 c.c.) as a solvent was used in the above reaction with the same quantities of the reactants, and the reaction was carried out either

heating at 95-100° for 2 hours or keeping the reaction mixture at room temperature for 72 hours, a brownish liquid was obtained on decomposition by ice and HCl. After nitrobenzene was removed by steam distillation, 2-acetyl-4-nitroresorcinol passed over with steam, which was collected as the main product (yield 1 g.). Traces of a yellow product could be recovered (m.p. 195-96°), but its identity could not be established due to insufficient quantity.

The residual liquid in the flask on filtering and cooling afforded a brownish yellow solid, which was crystallised from dilute ethanol in yellow needles; m.p. and the mixed m.p. with an authentic specimen of 2:6-diacetyl-4-nitroresorcinol (IV: R = Me), 139-40°.

Formation of 2:6-*Diacetyl-4-nitroresorcinol* (IV: R=Me) *by Nitration.*—2:6-Diacetylresorcinol (V: R=Me) (1 g.), isolated as one of the products in the Fries migration of resorcinol diacetate by aluminium chloride (3.3 *M*) in nitrobenzene at 100° for 3 hours (cf. Baker, *J. Chem. Soc.*, 1934, 1684), was dissolved in acetic acid (15-20 c.c.) and cooled in ice. A cooled mixture of HNO_3 (*d* 1.42, 5 c.c.) and H_2SO_4 (*d* 1.84, 5 c.c.) was added dropwise under stirring. After one hour, the reaction mixture was diluted with ice-water and the solid obtained was crystallised from dilute ethanol, m.p. 139-40°, yield 0.5 g. (Found : C, 49.91; H, 3.75; N, 5.77. $C_{10}H_9O_6N$ requires C, 50.02; H, 3.76; N, 5.85%). It is soluble in sodium hydroxide with a bright yellow colour and develops a deep orange-red colour with ethanolic ferric chloride. It is soluble in common organic solvents. The other diketones described below also responded to these tests.

2:4-*Dinitrophenylhydrazone* of the above diketone was prepared as usual as a yellow powder from acetic acid, m.p. 276° (decomp.). (Found : N, 20.74. $C_{22}H_{17}O_{12}N_9$ requires N, 21.03%).

Fries Rearrangement of 4-*Nitroresorcinol Dipropionate*

4-*Nitroresorcinol dipropionate* (II : R = Et) was prepared by heating a mixture of (I, 5 g.), thionyl chloride (20 c.c.) and propionic acid (20 c.c.) at 80° on a water-bath for 3 hours. After the evolution of HCl gas had ceased, the mixture was diluted with ice-water and treated with dilute NaOH till alkaline. It was then extracted with ether, dried over Na_2SO_4, ether removed and distilled as a pale yellow liquid at 170-73° |0.5 mm. (Found : N, 5.66. $C_{12}H_{13}O_6N$ requires N, 5.24%).

Formation of 2-*Propionyl-4-nitroresorcinol* (III: R = Et) *and* 2:6-*Dipropionyl-4-nitroresorcinol* (IV: R = Et).—The heating of the ester (II, 3 g., 1 *M*) with aluminium chloride (5 g., 3.3 *M*) at 100° for 3 hours afforded a solid after the usual treatment. It was crystallised from ethanol as yellow needles, m.p. 115-16°, yield 0.6 g. It was identified as 2-propionyl-4-nitroresorcinol (III: R = Et) by direct comparison with an authentic sample (Naik *et al., loc. cit.*).

The above reaction, when carried out as in (b), in nitrobenzene (25 c.c.) afforded (III, 1 g.) and also 2:6-dipropionyl-4-nitroresorcinol (IV: R = Et) as a non-steam-volatile residue. It was crystallised from dilute ethanol in shining yellow needles, m.p. 132-33°, yield 0.1 g. Mixed m.p. with an authentic sample remained undepressed.

Formation of 2:6-*Dipropionyl*-4-*nitroresorcinol* (IV:R=Et) *by Nitration.*—2:6-Dipropionylresorcinol (V:R=Et, 1 g.), isolated as one of the products of the Fries migration of resorcinol dipropionate, was nitrated as before. The brown solid was crystallised from ethanol as shining yellow needles, m.p. 132-33°, yield 0.5 g. (Found : C, 54.39 ; H, 4.81 ; N, 5.19. $C_{12}H_{13}O_6N$ requires C, 53.99 ; H, 4.6 ; N, 5.24%).

The 2:6-*dinitrophenylhydrazone* of the diketone was crystallised from acetic acid as a yellow powder, m.p. 255° (decomp.). (Found : N, 20.10. $C_{24}H_{21}O_{12}N_8$ requires N, 20.09%).

Fries Rearrangement of 4-*Nitroresorcinol Dibutyrate*

4-*Nitroresorcinol dibutyrate* (II:R=Pr^n) was prepared from (I, 5 g.) similarly as the dipropionate. After the usual treatment, the yellow thick liquid was obtained at 178-80°|0.5 mm. (Found : N, 5.07. $C_{14}H_{17}O_6N$ requires N, 4.75%).

Formation of 2-*Butyryl*-4-*nitroresorcinol* (III:R=Pr^n).—A solution of the dibutyrate (3 g., 1 *M*) and aluminium chloride (4.5 g., 3.3 *M*) in nitrobenzene (25 c.c.) was heated at 110-20° for 2 hours or was kept at room temperature for 72 hours. After the usual treatment, 2-butyryl-4-nitroresorcinol (III: R=Pr^n) was isolated as the steam-volatile product and also from the residual distillate. It was crystallised from ethanol as light yellow plates, m.p. and the mixed m.p. with an authentic sample, 78° (Naik *et al.*, *loc. cit.*). Traces of 4-nitroresorcinol could be recovered on working up the residual liquids. No diketone was isolated even in the absence of the solvent as in (*a*).

Fries Rearrangement of 4-*Nitroresorcinol* 1-*Monobenzoate* (VI) *and* 3-*Monobenzoate* (VII)

The mixture of the monobenzoates obtained by the nitration of the crude resorcinol monobenzoate was separated by extraction with chloroform in which 3-benzoate was less soluble (cf. Kaufmann and Kugel, *loc. cit.*).

Formation of 2-*Benzoyl*-4-*nitroresorcinol* (III:R=Ph).—A mixture of 4-nitroresorcinol 1-monobenzoate (VI:m.p. 124°, 3 g., 1 *M*) and aluminium chloride (3.5 g., 2.2 *M*) was heated at 130-40° for 2 hours. After the usual treatment the yellow solid obtained was washed with $NaHCO_3$ solution and crystallised from ethanol as small orange prisms, m.p. 159-60°, yield 0.5 g. The mixed m.p. with the authentic sample remained undepressed. Small amounts of the benzoic acid and 4-nitroresorcinol were recovered from the residual liquids.

The *same* reaction in nitrobenzene (25 c.c.) at 100° for 2 hours also furnished the same product in good yield (1.3 g.). No diketone could be obtained on working up the residual tailings.

Under the above conditions (VII) afforded the same monoketone, identified by the mixed m.p. No other ketonic product could be recovered.

Fries Rearrangement of 4-*Nitroresorcinol Dibenzoate*

4-*Nitroresorcinol dibenzoate* (II:R=Ph) was prepared by re-benzoylation the crude mixture of the 4-nitroresorcinol monobenzoates (6 g.) by benzoyl chloride (10 c.c.) in pyridine (5 c.c.) and heating for 2 hours on a water-bath. It was crystallised from acetic acid in pale yellow needles, m.p. 110°, yield 3 g.

Rearrangement of (II:R=Ph) : *Formation of* 2-*Benzoyl*-4-*nitroresorcinol* (III:R=Ph)

The mixture of (II:R=Ph, 3 g., 1 *M*) and aluminium chloride (3.6 g., 3.3 *M*) was heated at 140° for 3 hours. After decomposition of the reaction mass, the yellow solid was crystallised from ethanol; m.p. and the mixed m.p. with the above sample, 159-60°. Some benzoic acid and 4-nitroresorcinol were recovered.

The reaction in nitrobenzene (20 c.c.) at 100° or at 140° for 2 hours also gave the same benzoylketone unaccompanied with any diketone.

Thanks are due to Srimati Saraswati Amin for the kind interest in the work and to Dr. R. M. Naik for supplying the authentic samples of 2-acyl-4-nitroresorcinols.

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ESTIMATION OF PALLADIUM BY α,β-DIOXIMINOACETOACET-*o*-CHLORANILIDE

By J. S. Dave and A. M. Talati

α,β-Dioximinoacetoacet-*o*-chloranilide precipitates Pd quantitatively as $PdC_{20}H_{18}N_6O_6Cl_2$. The gravimetric estimation of palladium by this reagent and the effect of *p*H, anions and cations on this estimation have been investigated.

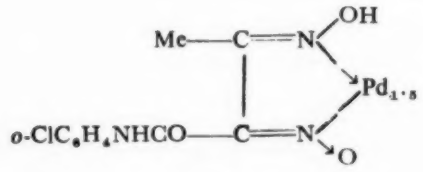
In continuation of our previous communication (this *Journal*, 1959, **36**, 179), we present herein the results of our investigations on the gravimetric estimation of palladium by α,β-dioximinoacetoacet-*o*-chloranilide. Palladium forms a yellow complex having the formula $Pd(C_{10}H_9N_3O_3Cl)_2$ with α,β-dioximinoacetoacet-*o*-chloranilide. Palladium is quantitatively precipitated from fairly acidic solutions (*p*H 0.4) in presence of various ions; however, an error is introduced in presence of nitrate ion even when the estimation is carried out from alkaline solution.

Experimental

α,β-Dioximinoacetoacet-*o*-chloranilide was prepared from acetoacet-*o*-chloranilide (Dave and Talati, *Curr. Sci.*, 1957, **26**, 326). 1% Alcoholic solution of this reagent was used in all the estimations. Solutions of palladium chloride and other reagents used are mentioned in the previous communication (*loc. cit.*).

Composition of the Complex.—The palladium complex was prepared and its composition was determined as discussed previously. (Found : Pd, 17.37, 17.23, 17.32. Calc for $PdC_{20}H_{18}N_6O_6Cl_2$: Pd, 17.32%).

The results suggest that the composition of the complex can be represented as



Procedure.—An aliquot quantity of palladium solution was diluted to about 200 c.c. with HCl (dil.) (*p*H was adjusted to about 0.4 to 0.7). To this solution was added, after warming, sufficient amount of 1% alcoholic solution of the reagent (1 g. reagent for 0.1 g. Pd). The precipitates were digested on the water-bath for about an hour, filtered, washed with water and dried at 110-20° to a constant weight. The precipitates were weighed as $PdC_{20}H_{18}N_6O_6Cl_2$, the factor for Pd being 0.1732. Some of the results are shown in Table I.

TABLE I

Pd taken.	Pd complex obtained.	Pd found.	Error.
8.62 mg.	49.6 mg.	8.59 mg.	−0.03 mg.
11.40	65.9	11.41	+0.01
13.06	75.7	13.11	+0.05
17.24	100.2	17.36	+0.12
21.94	127.2	22.03	+0.09

Effect of pH.—In order to study the *p*H range over which palladium can be completely precipitated by this reagent, estimation of palladium was carried out in solutions having different *p*H values. The *p*H values of the undiluted filtrates were determined by L and N *p*H meter. The results, recorded in Table II, show that palladium is completely precipitated by this reagent above *p*H 0.1 (and at least up to *p*H 10.1).

TABLE II

*p*H	..	0.12	0.60	8.94	10.10
Pd taken (mg.)	..	11.40	8.62	8.62	11.40
Pd found (mg.)	..	11.36	8.59	8.59	11.47

Effect of Anions and Cations.—Palladium was estimated in presence of different cations at *p*H 0.4 to 0.7 (precipitates were twice washed with dilute HCl and then with water). The results are recorded in Table III.

TABLE III

Salt added.		Palladium. Taken.	Found.	Error.
$HgCl_2$	1.36 g.	8.62 mg.	8.57 mg.	−0.05 mg.
$ZnSO_4$	1.43	8.62	8.68	+0.06
$CdSO_4$	0.064	8.62	8.68	+0.06
$CrCl_3$	0.134	8.62	8.64	+0.02
$FeCl_3$	0.135	8.62	8.73	+0.11
$SbCl_3$	0.113	8.62	8.73	+0.11
$CoCl_2$	0.119	8.62	8.66	+0.04
$SnCl_2$	0.113	8.62	8.73	+0.11
$CaCl_2$	1.10	11.40	11.41	+0.01
$BaCl_2$	1.50	11.40	11.38	−0.02
$MgCl_2$	0.50	11.40	11.43	+0.03

Cation	added.	*p*H.	Palladium. Taken.	Found.	Error.
Ni (II)	6.81 mg.		5.87	5.96	+0.09 mg.
Ni (II)	13.22		5.87	5.82	−0.05
Cu (II)	15.25		5.87	5.94	+0.07
Salt added.					
$NaCO_2CH_3$	2.0	0.7	8.62	8.59	−0.03
$NaNO_3$	2.0	10.2	8.62	9.70	+1.08
K_2SO_4	2.0	2.4	11.40	11.45	+0.05

Similarly the estimation was carried out in presence of different anions at different *p*H values. The results in Table III indicate that the metals under investigation cause little or no interference to the estimation of palladium, but that nitrate ion interferes even when the estimation is carried out from alkaline solutions.

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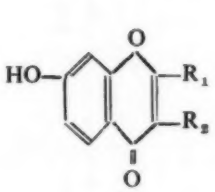
FRIES TRANSFORMATION AND FRIEDEL-CRAFTS REACTION. PART III. FRIEDEL-CRAFTS ACYLATION OF SOME HYDROXYCHROMONES

By S. M. Parikh and V. M. Thakor *

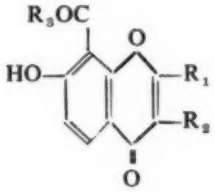
The Friedel-Crafts acylations have been carried out with several 7-hydroxychromones. The resulting 7-hydroxy-8-acylchromones (55-70% yield) have been smoothly oxidised using hydrogen peroxide (Dakin) to the corresponding 7:8-dihydroxychromones. The method appears to be useful for the preparation of *ortho*-dihydroxychromones.

Application of the Friedel-Crafts reaction to chromones has not been investigated, though the Fries rearrangement has been successfully applied to some hydroxychromone esters. As these hydroxyacylchromones on the Dakin oxidation would furnish an alternative method for *ortho*-dihydroxychromones (cf. Seshadri, *et al.*, *Proc. Indian Acad. Sci.*, 1939, **9A** 7; 1948, **28A**, 99), the Friedel-Crafts acylation of hydroxychromones and the subsequent Dakin oxidation of the hydroxyacylchromones have been undertaken

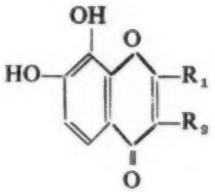
7-Hydroxy-2:3-dimethylchromone (IA) on the Friedel-Crafts reaction with acetic anhydride afforded 7-hydroxy-2:3-dimethyl-8-acetylchromone (IIA : R_3 = Me) in 65% yield. Oxidation of the 8-acetylchromone in alkaline hydrogen peroxide (Dakin) at 0° yielded 7:8-dihydroxy-2:3-dimethylchromone (IIIA).



(I)



(II)



(III)

[A : $R_1 = R_2 =$ Me. B : $R_1=$ Me ; $R_2 =$ H. C : $R_1 =$ Ph ; $R_2 =$ H]

Similarly on the Friedel-Crafts propionylation and benzoylation, the above chromone (IA) furnished the corresponding 8-propionyl- (IIA : R_3 = Et) and 8-benzoyl-(IIA : R_3 = Ph) chromones. The Dakin oxidation of the 8-propionylchromone (IIA: R_3 = Et) afforded only poor yields of the corresponding 7:8-dihydroxychromone (IIIA).

The similar Friedel-Crafts acetylation of 7-hydroxy-2-methylchromone (IB) and 7-hydroxyflavone (IC) furnished the 8-acetylchromones (IIB, IIC) in excellent yields. The 8-acetylchromones on the Dakin oxidation furnished the corresponding 7:8-dihydroxychromones (IIIB, IIIC).

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TABLE I

Friedel-Crafts reaction on chromones.

No.	Chromones.	Acylating agent.	$AlCl_3$.	Temp.	Period.	Product.	Yield.	M.P.	Reference.
1.	7-Hydroxy-2:3-dimethyl	Ac_2O	4.4 *M*	140-45°	1½ hrs.	8-Acetyl	65%	215°	1
2.	Do	Pr_2O	4.4	155-60°	1½	8-Propionyl	55	163°	2
3.	Do	PhCOCl	3.3	170-75°	2	8-Benzoyl	60	208°	1
4.	7-Hydroxy-2-methyl	Ac_2O	4.4	135-40°	1½	8-Acetyl †	70	187°	3
5.	7-Hydroxy-2-phenyl	,,	4.4	155-60°	2	8-Acetyl	60	212°	*
6.	5-Hydroxy-2-phenyl	,,	4.4	145-50°	1½	6-Acetyl	55	200°	4
7.	5:7-Dihydroxy-2:3-dimethyl	,,	4.4	155-60°	2	6-(8)-Acetyl	50	165°	§

† Crystallised from 75% ethanol.

* Found : C, 72.7 ; H, 4.4. $C_{17}H_{12}O_4$ requires C, 72.8 ; H, 4.3%.

§ Found : C, 63.0 ; H, 4.9. $C_{18}H_{14}O_5$ requires C, 62.9 ; H, 4.9%.

1. Kelkar and Limaye, *Rasayanam*, 1939, **1**, 183.
2. Wittig, *Ber.*, 1926, **59**, 116.
3. Wittig *et al.*, *Annalen*, 1925, **446**, 105.
4. Baker, *J. Chem. Soc.*, 1934, 1953.

5-Hydroxyflavone and 5:7-dihydroxy-2:3-dimethylchromone on similar acetylation yielded the corresponding 6-acetyl and 6- or (8)-acetyl derivatives. The Dakin oxidation of these hydroxyacetylchromones was, however, unsuccessful (cf. Baker, *J. Chem. Soc.*, 1934, 1953).

In general, the Friedel-Crafts acylation can smoothly provide 60-70% yield. 7-Hydroxy-8-acylchromones can be smoothly oxidised by using alkaline hydrogen peroxide to the corresponding 7:8-dihydroxychromones (55-70%). Thus acetylation and the subsequent Dakin oxidation provide an alternative method for the preparation of *ortho*-dihydroxychromones.

EXPERIMENTAL

Friedel-Crafts Reaction of Hydroxychromones.—To an intimate mixture of hydroxychromones (1.0 *M*) and anhydrous aluminium chloride, the acid anhydride or chloride (1.1 *M*) was added and the reaction mixture heated at the requisite temperature for the requisite period. It was cooled and ice and HCl (conc.) were added. The acylchromone obtained was collected, washed and crystallised from ethanol (except where otherwise stated in Table I).

When the above reaction was carried out in nitrobenzene as solvent, lower yields were obtained. All the products developed deep red coloration with alcoholic ferric chloride.

TABLE II

Dakin oxidation of hydroxyacylchromones.

No.	Chromone.	Period.	Product : chromone.	Crystn.	Yield.	M.P.	Reference.
1.	7-Hydroxy-2:3-dimethyl-8-acetyl	3 hrs.	7:8-Dihydroxy-2:3-dimethyl	a	0.15 g.	234°	5
§ 2.	7-Hydroxy-2:3-dimethyl-8-propionyl	6	Do	a	0.03 *	234°	5
3.	7-Hydroxy-2-methyl-8-acetyl	3	7:8-Dihydroxy-2-methyl	b	0.15	242°	6
4.	7-Hydroxy-2-phenyl-8-acetyl	3	7:8-Dihydroxy-2-phenyl	b	0.13	246°	6
§ 5.	5-Hydroxy-2-phenyl-6-acetyl	3	Original	..	..	..	4
§ 6.	5:7-Dihydroxy-2:3-dimethyl-6(8)-acetyl	3	Original	..	..	..	

(a) 75 % Ethanol; (b) 95 % ethanol.
§ Pyridine (4 c.c.) was added to dissolve the sodium salt.
* Original chromone (0.13 g.) was recovered.

5. Canter, Martin and Robertson, *J. Chem. Soc.*, 1931, 1878.
6. Venkataraman, *ibid.*, 1929, 2219.

Dakin Oxidation of Hydroxyacylchromones.—The above hydroxyacylchromone (0.25 g.) in 2% aqueous NaOH (3 c.c.) and water (5 c.c.) at 0° was treated with 3% H_2O_2 (3 c.c.) and kept at that temperature for the requisite period. It was then acidified and the dihydroxychromone obtained was crystallised. All the dihydroxy compounds developed a green coloration with alcoholic ferric chloride.

Fries Rearrangement of 7-Acetoxyflavone.—7-Acetoxyflavone (2.8 g.) and powdered anhydrous aluminium chloride (4.4 g.) were heated at 55-60° for 2 hours. The reaction mixture was decomposed with ice and hydrochloric acid. 7-Hydroxy-8-acetylflavone was collected, washed and crystallised as colorless shining needles, m.p. 212°, yield 1.7 g.

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PHYSICO-CHEMICAL STUDIES ON METALLIC TUNGSTATES. PART IV. ELECTROMETRIC STUDIES ON MERCURIC TUNGSTATE

By R. S. Saxena and C. M. Gupta

The formation and precipitation of mercury tungstate have been studied conductometrically and potentiometrically. From the results obtained the composition is best expressed by the formula $HgO.WO_3$ between *p*H 3 and 4. Effect of electrolytes and non-electrolytes has also been studied.

It is well known that precipitation of metallic tungstates is affected by a number of factors, mainly aggregation of tungstate ion, *p*H of the medium, age and formation of various polymers. In view of this, analytical methods fail to provide a correct composition of the metallic tungstate precipitated, on adding a soluble metallic salt to sodium tungstate. A review of literature reveals that the reaction between $Hg(NO_3)_2$ and Na_2WO_4 has hardly been studied by one or two authors by analytical methods (Wirtz, *Metall. u. Erz.*, 1944, **41**, 84; Blumenthal, *ibid.*, 1942, **39**, 1942). No attempt appears to have so far been made to study the present reaction by electrometric methods. Hence in continuation of our physico-chemical studies on metallic tungstates (this *Journal*, 1958, **35**, 830; *Curr. Sci.*, 1958, **27**, 436; *J. Sci. Ind. Res.*, 1958, **17B**, 136, 503; *Z. physikal. Chem.*, 1959, **19**, 94) an attempt has been made to investigate thoroughly the present reaction by potentiometric and conductometric methods which supply rather conclusive views regarding the composition of the metallic tungstate precipitated.

Experimental

Na_2WO_4 and $Hg(NO_3)_2$ of A. R. quality were used. The solutions were prepared in conductivity water. Na_2WO_4 was estimated as the oxinate, $WO_2(C_9H_6ON)_2$.

A solution of $Hg(NO_3)_2$ was prepared in minimum quantity of A. R. nitric acid and was standardised against standard KCNS. The procedures for conductometric and potentiometric titrations are the same, as described previously (this *Journal*, 1953, **35**, 617; 1958, **35**, 830). A salt bridge of potassium nitrate and agar and a saturated calomel electrode were used as the reference half cell throughout the potentiometric measurements.

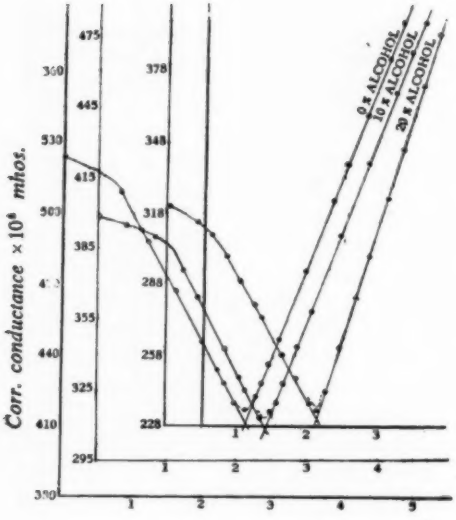
Discussion

It is really very interesting to find normal mercury tungstate precipitating in acidic medium (*p*H range 3-4), where generally one expects larger amounts of polytungstate anions in preponderance to normal WO_4^{2-} (Remy, "Treatise on Inorganic Chemistry", Elsevier Publishing Co., London, 1956, p. 177). It is prob-

able that the concentration of normal WO_4^{2-} is sufficient to reach the solubility product of $HgWO_4$ at the above H^+-ion concentration.

FIG. 1

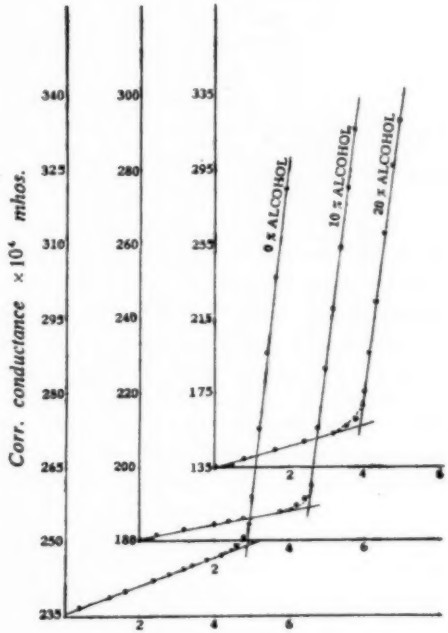
Direct conductometric titrations.



0.04 *M*-Na_2WO_4 *added to* 20 c.c. *of* 0.005 *M*-$Hg(NO_3)_2$ *in c.c.*

FIG. 2

Reverse conductometric titrations.



0.2 *M*-$Hg(NO_3)_2$ *added to* 20 c.c. *of* 0.05 *M*-Na_2WO_4 *in c.c.*

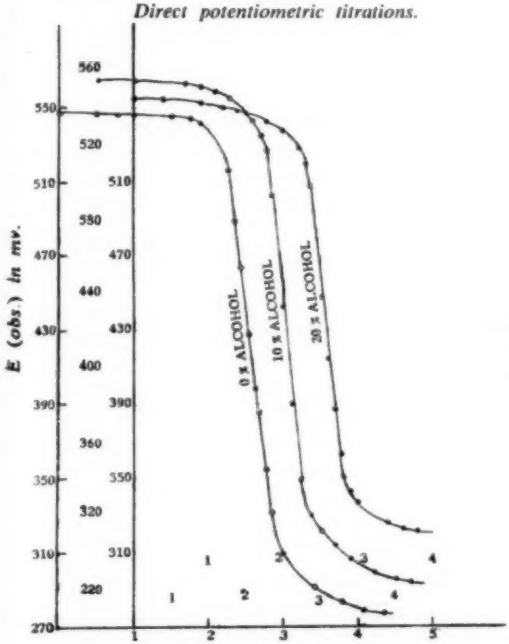
One may observe from the Figs. 1 and 2, that both direct and reverse conductometric titration curves yield one break only, corresponding to the formation and precipitation of normal mercury tungstate, $HgO.WO_3$. In direct titrations, on adding Na_2WO_4 to $Hg(NO_3)_2$, the conductivity decreases in the beginning as the faster moving Hg^{2+} is replaced by Na^+. After complete precipitation of $HgWO_4$, the conductance again rises as the ionic mobility of $WO_4^{2-} > NO_3^-$. The precipitated $HgWO_4$ does not contribute to the conductance. In reverse titrations, the conductance slightly decreases as faster moving WO_4^{2-} is replaced by slower moving NO_3^- and after the end-point, the conductance sharply rises due to excess of Hg^{2+}. Addition of alcohol improves the results slightly.

It will be observed from Figs. 3 and 4, that the formation of mercury tungstate can be successfully investigated by E.M.F. measurements also. In reverse titrations (Fig. 4), the E.M.F. rises gradually from the beginning of the reaction, becoming steady after waiting for 2 minutes in each reading till an upward jump in potential is observed at the end-point beyond which E.M.F. becomes constant

again. Both the direct and reverse curves are regular in shape and a pronounced maxima in dE/dV is obtained at the point of equivalence.

FIG. 3

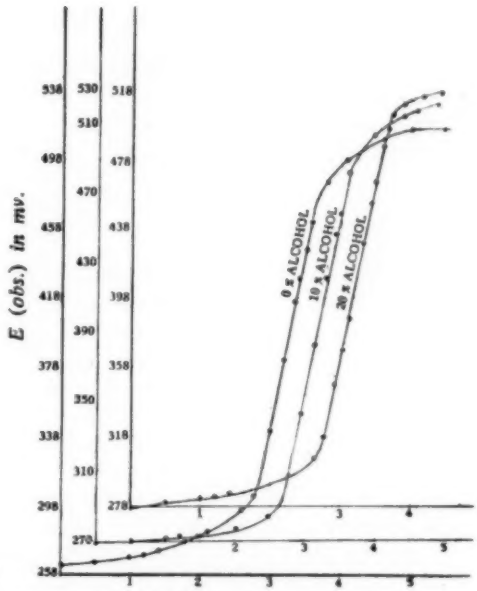
Direct potentiometric titrations.



0.2 *M*-Na_2WO_4 *added to* 20 c.c. *of* 0.025 *M*-$Hg(NO_3)_2$ *in c.c.*

FIG. 4

Reverse potentiometric titrations.



0.1 *M*-$Hg(NO_3)_2$ *added to* 20 c.c. *of* 0.0166 *M*-Na_2WO_4 *in c.c.*

Alcohol and electrolytes like KNO_3 and NH_4NO_3 have neither any effect on the shape of the curves nor on the end-point.

TABLE I

Summary of conductometric titrations.

Na_2WO_4.	$Hg(NO_3)_2$.	Point showing break. In aq. solution. Calc.	Obs.	In alcoholic solution Calc.	Obs.	
			Direct.			
M|5	*M*|40	2.5 c.c.	2.55 c.c	2.25 c.c.	2.30 c.c.	in 10% alc.
				2.00	2.05	20% alc.
M|10	*M*|100	2.0	2.10	1.80	1.90	10% alc.
				1.60	1.60	20% alc.
M|25	*M*|200	2.5	2.60	2.25	2.35	10% alc.
				2.00	2.05	20% alc.
			Reverse.			
M|20	*M*|5	5.0	*4.9*	4.50	4.40	10% alc.
				4.00	3.95	20% alc.
M|100	*M*|20	*4.0*	*3.9*	3.60	3.50	10% alc.
				3.20	3.15	20% alc.
M|300	*M*|50	3.33	3.25	3.00	2.90	10% alc.
				2.66	2.60	20% alc.

Tables I and II reveal that observed titre value of Na_2WO_4 is slightly higher than the theoretical value in direct titrations, whereas that of $Hg(NO_3)_2$ is a little less. The slight discrepancy between observed and calculated amounts of one reactant required for 20 c.c. of the other probably rises due to hydrolytic nature of Na_2WO_4, which undergoes hydrolysis as :

$$2WO_4^{2-} + H.OH \rightleftharpoons W_2O_7^{2-} + 2OH^-$$

supporting the views of Kuan Pan *et. al.* (*Bull. Chem. Soc. Japan*, 1953, **26**, 131). In direct titrations less normal WO_4^{2-} are available due to hydrolysis and hence a little more of it is required, whereas in reverse, a little less volume of $Hg(NO_3)_2$ is required than theoretical value for the precipitation of $HgO.WO_3$.

TABLE II

Summary of potentiometric titrations.

Na_2WO_4.	$Hg(NO_3)_2$.	Points of equivalences [Na_2WO_4 or $Hg(NO_3)_2$ required for the formation of $HgO.WO_3$] Calc.	Obtained in presence of alcohol. 0%	10%.	20%.
		Direct.			
M|10	*M*|100	2.0 c.c.	2.05 c.c.	2.05 c.c.	2.00 c.c.
M|20	*M*|100	4.0	4.10	4.10	4.00
M|5	*M*|40	2.5	2.60	2.55	2.55
		Reverse.			
M|100	*M*|20	4.0	3.90	3.95	3.95
M|240	*M*|40	3.33	3.20	3.20	3.25

The precipitated mercury tungstate when analysed for Hg^{2+} and tungsten contents provided results, in agreement with those obtained from electrometric methods.

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SPECTROPHOTOMETRIC STUDIES ON THE STABILITY OF COPPER BIGUANIDE CHELATES

By Manoj Mohan Ray and Priyadaranjan Rây

The successive instability constants of some copper biguanide complexes have been determined by spectrophotometric measurements made in aqueous medium at 30°±2°. The order of stability agrees with that reported earlier on the basis of potentiometric measurements. The dependence of chelate stability upon the basic strength of the ligand has been discussed.

In some previous publications the stability constants of a few biguanide complexes of cobalt(III) (De, Ghosh and Rây, this *Journal*, 1950, **27**, 493), chromium(III) (Bandyapadhaya, Ghosh and Rây, *ibid*., 1952, **29**, 157) and silver (III) (Sen, Ghosh and Rây, *ibid*., 1950, **27**, 619) were reported, mainly on the basis of potentiometric measurements. A more or less systematic study was made on the copper(II) and nickel(II) complexes of biguanide and substituted biguanides by Das Sarma and Rây (*ibid*., 1956, **33**, 841) with a view to obtaining some quantitative informations regarding the influence of the ligand or of the metal atom on the chelate stability. The stabilities of various biguanide complexes with one and the same metal (copper or nickel) were found to be more or less of the same order and no simple relationship between the basic strength of the different biguanides with the stability of their copper or nickel complexes could be found.

In fact, it has been observed by some authors that for certain groups of ligands of sufficient structural similarity, there exists a linear relationship between the negative logarithm of their dissociation constants and the logarithm of the formation constants of their complexes with a given metal ion (Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401; Bjerrum, *Chem. Rev.*, 1950, **46**, 381; Van Uitert *et al*., *J. Amer. Chem. Soc*., 1953, **75**, 457). Others have, however, failed to confirm this relationship between the two (Rây, this *Journal*, 1955, **32**, 141; Das Sarma and Rây, *ibid*., 1956, **33**, 841; Jones *et al*., *J. Chem. Soc*., 1958, 2001). The chelate stability constants have also been found to vary as a function of such atomic characteristics as ionic radii and second ionisation potential of the gaseous atoms (Irving and Williams, *Nature*, 1948, **162**, 746) or electronegativity (Izatt *et al*., *J. Phys. Chem*., 1955, **59**, 80). With a view to confirming the previous results of potentiometric studies, determination of the stability constants of the biguanide chelates by spectrophotometric measurements was undertaken. Biguanide complexes of Cu^{II} and Ni^{II}, typical members of the metal ion series, as defined by Irving and Williams (*J. Chem. Soc*., 1953, 3192), were chosen for the purpose. The present paper is confined to the study of copper chelates of biguanide, methylbiguanide, phenylbiguanide and ethylenedibiguanide.

In the system of copper biguanide complexes, the equilibria for successive formation or decomposition are sufficiently far apart for any overlapping to occur.

The variation of their absorption spectra with *p*H shows the existence of two distinct equilibria, one between aquo-cupric ion and copper *mono*-biguanide and the other between copper *mono*-biguanide and copper *bis*-biguanide. The simultaneous occurrence of more than two absorbing species in one and the same spectral range is therefore excluded. Such two-component systems of absorbing species can be analysed from their absorption spectra, and the concentration of one of the coloured species formed at equilibrium can be easily calculated from their molar extinction coefficients. Thus, the optical density, D, of an equilibrium solution, at a particular wave-length at which both the species, A and B, have appreciable absorption, is given by

$$D = \varepsilon_A C_A + \varepsilon_B C_B$$

where ε and C signify respectively the molar extinction coefficients and concentrations of the coloured species. Since $C_A + C_B = C$, the concentration of the complex or the metal ion initially taken, as the case may be, the above equation can be rearranged to

$$C_A = \frac{D - \varepsilon_B C}{\varepsilon_A - \varepsilon_B}$$

Decomposition of Copper Biguanide Complexes

Copper biguanide complexes react with acids in aqueous solution and suffer stepwise dissociation in the following manner :

$$\text{I.} \quad Cu(BigH)_2^{2+} + H^+ \rightleftharpoons Cu(BigH)^{2+} + BigH_2^+$$

$$\text{II.} \quad Cu(BigH)^{2+} + H^+ \rightleftharpoons Cu^{2+} + BigH_2^+$$

where $BigH_2^+$ is the conjugate acid of the biguanide base BigH, corresponding to the uptake of one proton. The molarity quotients for the above decomposition reactions are given by

$$k'_2 = \frac{[Cu(BigH)^{2+}]\ [BigH_2^+]}{[Cu(BigH)_2^{2+}]\ [H^+]} \quad ; \quad k'_1 = \frac{[Cu^{2+}]\ [BigH_2^+]}{[Cu(BigH)^{2+}]\ [H^+]}$$

the square brackets representing concentrations. Low concentration of the reactants has been used in the presence of a large excess of a highly ionised neutral salt in order to minimise the variation of the activity coefficients of the individual reacting species. In view, however, of the favourable valency relationship of the ions involved, there will be no appreciable change in the value of the constant if molar concentratons be substituted for activities.

Let the concentration of the complex initially taken $= C$, and at equilibrium

$$[Cu(BigH)_2^{2+}] = C_2,$$

$$[Cu(BigH)^{2+}] = C_1,$$

the concentration of the remaining cupric ion $=\Sigma Cu^{2+}$ and the total concentration of non-complex-bound biguanide $=x$. In the first step of the equilibria, when ΣCu^{2+} is negligible,

$$C = C_1 + C_2$$
$$x = C_1 = C - C_2$$
$$\therefore \quad k'_2 = \frac{(C - C_2)\,[BigH_2^+]}{C_2\,[H^+]}.$$

In the second step of the equilibria, when C_2 is negligible,

$$C = C_1 + \Sigma Cu^{2+}$$
$$x = 2C - C_1$$
$$\therefore \quad k'_1 = \frac{[Cu^{2+}]\,[BigH_2^+]}{C_1\,[H^+]}.$$

C_2, C_1 and ΣCu^{2+} are evaluated by optical analysis. $[H^+]$ is known from the measured pH of the solutions. $[Cu^{2+}]$ can be calculated from ΣCu^{2+} in the following way :

$$\Sigma Cu^{2+} = [Cu^{2+}] + [CuCl^+]$$
$$= [Cu^{2+}] + [Cu^{2+}]\,[Cl^-]\,K_{CuCl^+}$$

(formation of the higher chloro-complexes being assumed to be negligible)

or
$$[Cu^{2+}] = \frac{\Sigma Cu^{2+}}{(1 + [Cl^-]\,K_{CuCl^+})}$$

where K_{CuCl^+} is the association constant of $CuCl^+$.

The concentration of $BigH_2^+$ can be evaluated from a knowledge of the acid dissociation constants of biguanides, using the following expression :

$$x = [BigH] + [BigH_2^+] + [BigH_3^{2+}]$$
$$= [BigH_2^+]\,\{k_{a_1}/[H^+] + 1 + [H^+]/k_{a_2}\}.$$

where k_{a_1} and k_{a_2} are the acid dissociation constants of the conjugate acids, $BigH_2^+$ and $BigH_3^{2+}$, of biguanide.

Now, the successive instability constants, k_2 and k_1, of the complex can be calculated from their corresponding decomposition constants, discussed above. Thus,

$$Cu(BigH)_2^{2+} \rightleftharpoons Cu(BigH)^{2+} + BigH$$

and
$$Cu(BigH)^{2+} \rightleftharpoons Cu^{2+} + BigH.$$

The instability constants

$$k_2 = \frac{[Cu(BigH)^{2+}]\,[BigH]}{[Cu(BigH)_2^{2+}]}$$
$$= \frac{[Cu(BigH)^{2+}]\,[BigH_2^+]}{[Cu(BigH)_2^{2+}]\,[H^+]} \times \frac{[BigH]\,[H^+]}{[BigH_2^+]} = k'_2 . k_{a_1}$$

and
$$k_1 = \frac{[Cu^{2+}]\,[BigH]}{[Cu(BigH)^{2+}]} = k'_1 .\ k_{a_1}.$$

The overall instability constant, K, corresponding to the reaction

$$Cu(BigH)_2^{2+} \rightleftharpoons Cu^{2+} + 2\ BigH$$

is given by

$$K = \frac{[Cu^{2+}]\ [BigH]^2}{[Cu(BigH)_2^{2+}]} = k'_2 .\ k'_1\ (k_{a_1})^2 .$$

Formation of Copper Biguanide Complexes

When solutions of cupric ion and biguanide hydrochloride are mixed, successive chelation takes place in the following way, depending upon the *p*H of the mixture.

$$\text{I.}\quad Cu^{2+} + BigH_2^+ \rightleftharpoons Cu(BigH)^{2+} + H^+$$

$$\text{II.}\quad Cu(BigH)^{2+} + BigH_2^+ \rightleftharpoons Cu(BigH)_2^{2+} + H^+ .$$

The association constants for the above reactions are

$$kf'_1 = \frac{[Cu(BigH)^{2+}]\ [H^+]}{[Cu^{2+}]\ [BigH_2^+]} = 1/k'_1$$

and

$$kf'_2 = \frac{[Cu(BigH)_2^{2+}]\ [H^+]}{[Cu(BigH)^{2+}]\ [BigH_2^+]} = 1/k'_2 .$$

Let α = initial cupric ion concentration and β = initial biguanide concentration.

I. When C_2 is negligible, $\alpha = \Sigma Cu^{2+} + C_1$ and $x = \beta - C_1$,

$$kf'_1 = \frac{(1 + [Cl^-]\ K_{CuCl^+})\ C_1\ [H^+]}{(\alpha - C_1)\ [BigH_2^+]}$$

II. When ΣCu^{2+} is negligible, $\alpha = C_1 + C_2$ and $x = \beta - C_1 - 2C_2$,

$$kf'_2 = \frac{C_2\ [H^+]}{(\alpha - C_2)\ [BigH_2^+]} .$$

The successive formation constants are, $kf_1 = kf'_1/k_{a_1}$ and $kf_2 = kf'_2/k_{a_1}$.

The overall formation constant corresponding to the reaction,

$$Cu^{2+} + 2\ BigH \rightleftharpoons Cu(BigH)_2^{2+}$$

is given by

$$Kf = \frac{[Cu(BigH)_2^{2+}]}{[Cu^{2+}]\ [BigH]^2} = \frac{kf'_1 \cdot kf'_2}{(k_{a_1})^2}$$

Decomposition of Copper Ethylenedibiguanide

Copper ethylenedibiguanide, where ethylenedibiguanide functions as a quadridentate ligand, suffers one-step dissociation as represented below :

$$Cu(A)^{2+} + 2H^+ \rightleftharpoons Cu^{2+} + AH_2^{2+}$$

where A represents a molecule of ethylenedibiguanide and AH_2^{2+}, the ethylenedibiguanidinium ion corresponding to the uptake of two protons. The equilibrium constant of the above reaction is given by

$$K' = \frac{[Cu^{2+}]\,[AH_2^{2+}]}{[Cu(A)^{2+}]\,[H^+]^2}.$$

The total amount of non-complex-bound ligand is given by

$$x = [A] + [AH^+] + [AH_2^{2+}] + [AH_3^{3+}] + [AH_4^{4+}]$$

where AH^+, AH_2^{2+}, AH_3^{3+} and AH_4^{4+} are the conjugate acids of the tetra-acidic ethylenedibiguanide base A. Now the concentration of AH_2^{2+} can be calculated from the following relation :

$$x = [AH_2^{2+}]\left\{\frac{k_{a_1}\,k_{a_2}}{[H^+]^2} + \frac{k_{a_2}}{[H^+]} + 1 + \frac{[H^+]}{k_{a_3}} + \frac{[H^+]^2}{k_{a_3}.k_{a_4}}\right\}$$

where k_{a_1}, k_{a_2}, k_{a_3} and k_{a_4} are the dissociation constants of the successive conjugate acids of ethylenedibiguanide.

Let the initial concentration of the complex $= C$, concentration of the complex at equilibrium $= C_2$, concentration of cupric ion at equilibrium $= \Sigma Cu^{2+}$.
Then $C = C_2 + \Sigma Cu^{2+}$ and $x = \Sigma Cu^{2+}$, giving

$$K' = \frac{\Sigma Cu^{2+}\,[AH_2^{2+}]}{(1 + [Cl^-]\,K_{CuC^+})\,C_2\,[H^+]^2}.$$

The instability constant, K, corresponding to the reaction

$$Cu(A)^{2+} \rightleftharpoons Cu^{2+} + A,$$

is given by

$$K = \frac{[Cu^{2+}]\,[A]}{[Cu(A)^{2+}]} = K'.\ k_{a_1}.k_{a_2}.$$

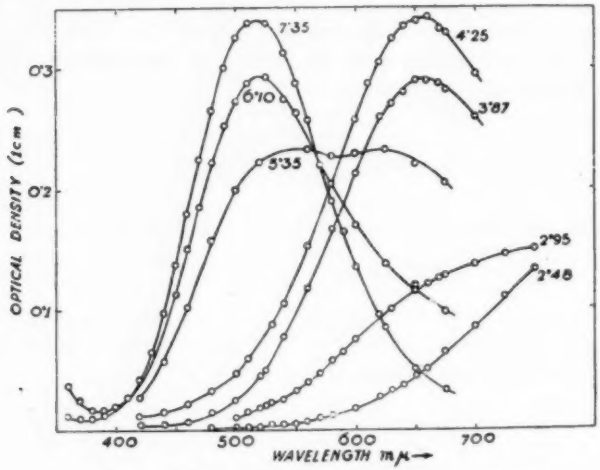
Absorption Spectra and Molar Extinction Coefficient

When a set of solutions of cupric ion and any biguanide hydrochloride in excess over the stoichiometric ratio, are made up at different *p*H, a gradual chromatic shift with *p*H is observed in the mixture (cf. Fig. 1). The green colour of aquo-cupric ion in the initial solutions changes to blue which is gradually intensified in successive solutions of increasing *p*H with an absorption peak at 650—660 mμ, typical of the *mono*-biguanide range 4.25—5.00. At higher *p*H the colour

gradually changes to purple and a new absorption peak appears at 520-530 mμ, characteristic of the *bis*-biguanide chelates. It reaches its maximum inten-

FIG. 1

Copper-biguanide system : variation of absorption spectra with pH.

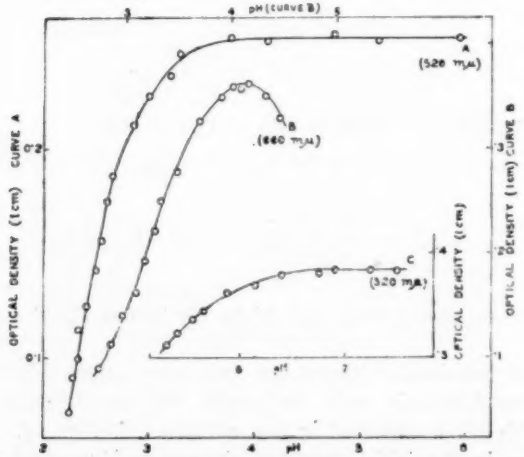


C_{copper}=0.01 *M* ; $C_{biguanide}$=0.02 *M* ; C_{KCl}=0.5 *M*.

sity at *p*H above 6.75. These spectral changes are exactly reversed when the pure *bis*-biguanide complex is decomposed with acids. On plotting the optical

FIG. 2

Evaluation of the extinction coeff.

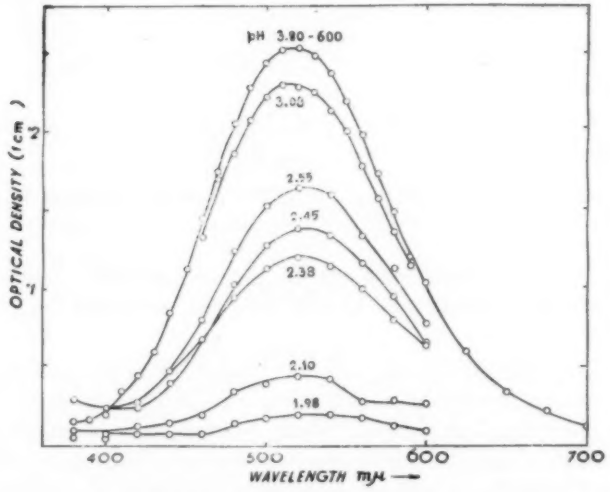


Curve A-Cu-ethylenedibiguanide : $C_{complex}$=0.00 *M* ; C_{KCl}=0.25 *M*.
B-Cu-*mono*-biguanide : C_{Cu}=0.01 *M* ; $C_{biguanide}$=0.03 *M* ; C_{KCl}=0.5 *M*.
C-Cu-*bis*-biguanide : same as in Curve B.

density for the wave-length of maximum absorption of copper *mono*-biguanide *versus* *p*H (cf. curve B, Fig. 2), the peak of the curve may be assumed to correspond to maximum formation of the relevant species. Hence, a fairly accurate value for its molar extinction coefficient can be derived from this optical density. A similar plot of optical density for the absorption maxima of the *bis*-biguanide chelate (cf. curve C, Fig. 2) shows a constant value at *p*H above 6.75, from which the molar extinction coefficient of the *bis*-biguanide complex can be calculated. The molar extinction coefficient of the copper *mono*-biguanide complex corresponding to the absorption maxima of the *bis*-complex, can be computed from the optical density of the solution (at the corresponding wave-length) in which the concentration of the former (*mono*-complex) is maximum, *i.e.*, where its formation is more or less complete.

FIG. 3

Copper-ethylenedibiguanide system : variation of absorption spectra with pH.



$C_{complex} = 0.005\ M$; $C_{KCl} = 0.25\ M$.

In the case of copper ethylenedibiguanide chelate, the formation or decomposition is a one-step reaction, as is evident from the variation of the absorption spectra with *p*H (cf. Fig. 3). The wave-length of maximum absorption for copper ethylenedibiguanide lies at 520 mμ. With gradual increase in the acidity of the solution, the absorbance falls without any shift in the absorption maxima. Ultimately (below *p*H 2) the absorption spectrum coincides with that of aquo-cupric ion. It is evident from the optical density *versus* *p*H curve (A in Fig. 2) that in aqueous solution copper ethylenedibiguanide suffer no dissociation until some acid is added. Hence the optical density of a solution of the complex chloride in water may furnish the molar extinction coefficient of the complex.

EXPERIMENTAL

TABLE I

Preparation of materials.

Materials.	Reference.
1. Biguanide acid sulphate $C_2N_5H_7.H_2SO_4,1.5H_2O$	Ostrogovich, *Chem. Zntrl.*, 1910, 1890.
2. Methylbiguanide acid sulphate $C_3N_5H_9.H_2SO_4,1.5H_2O$	Reibenschuh, *Monatsh.*, 1883, **4**, 394.
3. Phenylbiguanide hydrochloride $C_6H_5C_2N_5H_6.HCl$	Smolka & Friedrich, *ibid.*, 1883, **4**, 227.
4. Ethylenedibiguanide acid sulphate $C_6N_{10}H_{16}.H_2SO_4,1.5H_2O$	Chakravarty & Rây, this *Journal*, 1944, **21**, 41.
5. Copper *bis*-biguanide chloride $[Cu(C_2N_5H_7)_2]\,Cl_2,2H_2O$	Rây & Bagchi, *ibid.*, 1939, **16**, 617.
6. Copper *bis*-methylbiguanide chloride $[Cu(C_3N_5H_9)_2]\,Cl_2,2.5H_2O$	Reibenschuh, *loc. cit.*
7. Copper *bis*-phenylbiguanide chloride $[Cu(C_8N_5H_{11})_2]\,Cl_2,H_2O$	Rây & Chakravarty, this *Journal*, 1941 **18**, 609.
8. Copper ethylenedibiguanide chloride $[Cu(C_6N_{10}H_{16})]Cl_2,1.5H_2O$	Rây & Ghosh, *ibid.*, 1943, **20**, 293.

Biguanide dihydrochloride solutions of definite strength were prepared by treatment of the corresponding acid sulphate with the calculated amount of standard barium chloride solution.

Decomposition Studies.—In the case of copper biguanide and copper ethylenedibiguanide compounds stock solutions of molarity 0.05—0.10 were prepared from their complex chlorides. A definite volume of the stock solution was taken in each of a number of 50 c.c. volumetric Jena flasks. Varying quantities of hydrochloric acid and definite amounts of potassium chloride were added to the flasks before the volumes were finally made up to the mark. Thus, a set of solutions with varying acidity was obtained. The solutions were kept for 48 hours at 30° for equilibrium. The *p*H values of the solutions were measured in a Cambridge bench type *p*H meter which was previously calibrated against two buffers of *p*H 4.00 and 7.00. The optical density of the solutions was measured in a Unicam SP 600 spectrophotometer. In the case of methyl- and phenylbiguanide complexes, no stock solutions could be prepared due to their lower solubility and definite quantities of the complex chlorides were directly weighed into each flask.

Formation Studies.—Solutions of cupric ion and the biguanide hydrochloride concerned were mixed in the molar ratio of 1:2 or 1:3, as the case may be. *p*H of the solutions was adjusted at different values by the addition of carbonate-free KOH solution. Ionic strength was maintained constant with potassium chloride.

The *p*H and optical density of the mixtures were measured after allowing the solutions to stand for 48 hours to attain equilibrium.

The results of all experimental measurements and the values of the reaction constants are assembled in Tables II and III.

TABLE II

Decomposition of copper biguanide.

$C = 0.01\,M$. KCl = 0.5 *M*. Temp. = 30°±2°. $\varepsilon_{bis} = 38.5$. $\varepsilon_{mono} = 9.6$.
Wave-length = 520 mμ.

*p*H.	*D*(1cm.)	$C_2 = \frac{D - \varepsilon_{mono} C}{\varepsilon_{bis} - \varepsilon_{mono}}$.	$C_1 = C - C_2 = x$ = $BigH_2$.	$k'_2 \times 10^{-3}$.
6.75	0.325	0.007923	0.002077	3.06
6.50	0.315	0.007577	0.002423	2.45
6.25	0.302	0.007129	0.002871	2.06
6.00	0.285	0.006540	0.003460	1.83
5.80	0.270	0.006020	0.003980	1.66
5.75	0.265	0.005848	0.004152	1.66
5.50	0.235	0.004809	0.005191	1.77
5.35	0.220	0.004290	0.005710	1.70
5.20	0.200	0.003598	0.006402	1.81
5.00	0.175	0.002733	0.007267	1.93

k'_2(average) = 1.99×10^3.

TABLE III

	Molar extin coeff.	k'_2.	k'_1.	kf'_2.	kf'_1.
Copper-biguanide	$\varepsilon_2 = 38.5$ (520 mμ) $\varepsilon_1 = 9.6$ (520) $\varepsilon_1 = 36.0$ (660)	1.99×10^3	2.71×10 (1.64×10)	0.60×10^{-3}	0.038 (0.062)
Copper-methyl-biguanide	$\varepsilon_2 = 40.0$ (520) $\varepsilon_1 = 10.9$ (520) $\varepsilon_1 = 36.0$ (660)	7.40×10^3	7.85×10		
Copper-phenyl-biguanide	$\varepsilon_2 = 65.3$ (550) $\varepsilon_1 = 32.0$ (550) $\varepsilon_1 = 42.2$ (650)	2.49×10^3	4.06×10 (3.06×10)	0.78×10^{-3}	0.024 (0.032)
Copper-ethylenedi-biguanide	$\varepsilon = 50.5$ (520)	$K' = 35.66$ (26.91)			
Aquo-cupric ion	$\varepsilon = 5.0$ (660) $\varepsilon = 4.0$ (650)				

The values given in parenthesis refer to those corrected for $CuCl^+$.

DISCUSSION

The potentiometric measurements of the stability constants of biguanide chelates were previously made without any consideration of the ionic strength. In the present investigation, the ionic strengths of the solutions were maintained constant wherever it was permitted by the solubility of the complex chloride concerned. The choice of the neutral salt was restricted to potassium chloride in view of the low solubility of the complex salts of other anions. In the presence of Cl^- ion some of the metal ion may be present as the chloro-complex, and any constants calculated for the chelation processes which ignore the presence of these chloro-complexes may be in error to a certain extent. Van Uitert *et all.* (*J. Amer. Chem. Soc.*, 1955, **75,** 2739) have shown that for a given metal ion and chelating agent, the measured formation constant increases as the anion present varies from Cl^- to NO_3^- to ClO_4^-. The absorption data for solutions containing copper(II) chloride (0.005—0.01 *M*), biguanide dihydrochloride (0.015—0.02 *M*) and potassium chloride (0.25—0.5 *M*), which encompass the wave-length range of 400-750 mμ supply no information relative to the presence or absence of any chloro-complex of copper (cf. Moeller, *J. Phys. Chem.*, 1944, **48,** 111). The interference due to the highly dissociated copper(II) chloro-complexes, $CuCl_n^{2-n}$ for $1<n\leq 4$ (Bjerrum, *Chem. Abst.*, 1947, **41,** 5003) may be ignored in the evaluation of the instability constants of $Cu(BigH)^{2+}$. However, from the value of the association constant of $CuCl^+$, reported by McConnel and Davidson (*J. Amer. Chem. Soc.*, 1950, **72,** 3164) and by Monk (*Trans. Faraday Soc.*, 1951, **47,** 285), it appears that an appreciable amount of the uncomplexed cupric ion will form this chlorine-co-ordinated species in the solutions studied. Accepting the value 1.30 ± 0.03 (25.2°) as the association constant of $CuCl^+$, determined by McConnel and Davidson (*loc. cit.*) at a constant ionic strength of 0.1, the values of the instability constant of $Cu(BigH)^{2+}$ have been corrected for the competing equilibrium

$$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+.$$

However, such correction does not change the values of the order of the instability constants in any significant way.

Although the solutions were equilibrated at 30°, the temperature of the solutions fluctuated to the extent of ±2° during optical measurements as there was no thermostatic arrangement in the spectrophotometer. The average temperature throughout the present experimentation has been reported as 30°±2°. The acid dissociation constants of biguanides employed in relevant calculations were those determined by Das Sarma (this *Journal*, 1952, **29,** 217). For it was observed that the values of k_{a_1} and k_{a_2}, redetermined in the temperature range 30°±2° and at constant ionic strength, differed very little from those reported earlier. There is, however, some uncertainty in figures for the concentration of the complex, especially on that part of the optical density *versus* *p*H curves where the absorbance changes comparatively little with change in *p*H. This is also likely to introduce a slight error. The values of the instability constants, under the conditions of the experiment even without the rigid control of temperature, are in fairly good agreement with those previously reported on the basis of potentiometric measurements, as shown in Table IV.

TABLE IV

	Overall instability constant		KCl.	Overall formation constant
	K.	*K**.		*Kf*.
Copper biguanide	4.92×10^{-19} (2.98×10^{-19})	4.54×10^{-19}	0.5 *M*	0.25×10^{19} (0.41×10^{19})
Copper methylbiguanide	7.65×10^{-18}	7.05×10^{-18}		
Copper phenylbiguanide	3.92×10^{-17} (2.96×10^{-17})	1.77×10^{-17}	0.25	0.51×10^{17} (0.67×10^{17})
Copper ethylenedibiguanide	2.83×10^{-23} (2.14×10^{-23})	2.22×10^{-23}	0.25	

The values given in parenthesis refer to those corrected for $CuCl^+$.
* The values refer to those reported by Das Sarma and Rây (*loc. cit.*).

From a comparison of their first acid dissociation constants the biguanides, employed as ligands in the present investigation, may be arranged as follows in the increasing order of their basic strength : Phenylbiguanide < methylbiguanide < biguanide < ethylenedibiguanide.

From a consideration of the instability constants, the corresponding copper complexes may be arranged in the increasing order of their stability as follows : copper-phenylbiguanide<copper-methylbiguanide<copper-biguanide<copper-ethylenedibiguanide. The apparent correlation between the basic strength of the ligand and the stability of the chelate, as indicated by the parallelism of the two series, is lost when the comparison is extended to other substituted derivatives of biguanide (cf. Das Sarma, *loc. cit.*). In the case of ethylenedibiguanide, two biguanide fragments are combined together by the ethylenic group and in the complex an additional ring is formed without materially altering the donor groups. The increased stability of its copper complex may be attributed partly to an increase of configurational entropy due to stable ring formation.

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COMPLEX COMPOUNDS OF PALLADIUM(II) WITH SUBSTITUTED BIGUANIDES

By Manoj Mohan Ray

Behaviour of Pd^{II} with a number of substituted biguanides, viz., methyl-, ethyl-, dimethyl-, phenyl- and benzylbiguanides and ethylenedibiguanide has been studied. Besides the complex bases, chloride, sulphate, nitrate, thiocyanate and palladothiocyanate have been described. The palladium biguanide complexes resemble the corresponding nickel complexes, but are much more stable and less soluble. The complex thiocyanates undergo an interesting transformation in presence of acids into palladium *bis*-biguanide palladothiocyanates. The complexes are diamagnetic and presumably involve dsp^2 hybrid bonds with a square planar configuration.

The chemistry of Pd^{II} resembles in many respects that of Ni^{II}, both having the same type of electronic configuration in the outermost shell *i.e.*, eight electrons in a *d*-shell. This fact naturally led to a study of palladium biguanide complexes (Rây and Ghosh, this *Journal*, 1943, **20**, 19), which have been found to resemble closely those of nickel in their chemical and magnetic behaviour. The present paper deals with the preparation and properties of a number of Pd^{II} complexes with methyl-, ethyl-, dimethyl-, phenyl- and benzylbiguanides as well as with ethylenedibiguanide.

When the alkaline solution of a biguanide acid sulphate is treated with that of sodium tetrachloropalladite(II) and the mixture is warmed, a light yellow solution is obtained. On keeping, this solution slowly deposits silky white crystals of the complex palladium base. It was, however, found more convenient to prepare these bases by digesting any of the complex salts with alkali. While biguanide and its methyl and ethyl derivatives, as well as ethylenedibiguanide, afford their complex palladium hydroxides, dimethyl, phenyl and benzyl derivatives, on the other hand, form only the anhydro-bases even at the room temperature. Palladium *bis*-biguanide and ethylenedibiguanide hydroxides also form their anhydro-bases at 115°, losing two molecules of hydroxylic water. Palladium methyl- and ethylbiguanide bases, when heated at 120°, lose only their water of crystallisation.

All the complex bases are almost insoluble in water; in aqueous suspension they react alkaline to litmus, and liberate ammonia from ammonium salts, forming the corresponding complex salts.

The complex sulphates are readily obtained as silky yellowish white crystals by treating a warm solution of the biguanide acid sulphate with that sodium chloropalladite. These are very sparingly soluble in cold water. The complex chlorides have been prepared by triturating the sulphates with barium chloride and concentrating the filtrate from the precipitated barium sulphate. In a few cases these have been prepared by digesting the complex bases with ammonium chloride or neutralising them with dilute hydrochloric acid. These are fairly soluble in water forming light yellow solutions, except those of ethylenedibiguanide and benzylbiguanide, which are rather sparingly soluble. The complex chlorides of phenylbiguanide and benzylbiguanide are also moderately soluble in alcohol. The aqueous solution of palladium phenylbiguanide chloride slowly turns turbid due possibily to the separation

of the complex anhydro-base by hydrolysis. The moderately soluble complex nitrates and thiocyanates were prepared from the chlorides by metathesis with the corresponding potassium salts. The interesting transformation, in acid solution, of palladium *bis*-biguanide thiocyanate into a palladothiocyanate with partial elimination of biguanide, was first observed by Rây and Ghosh (*loc. cit.*). The complex thiocyanates of the substituted biguanides also behave in the same manner.

Conductivity measurements of some of the complex salts have been made in aqueous solution (vide Table II). The molecular conductivity values are consistent with the formulation of the complex as a bivalent cation. The magnetic susceptibilities of the palladium biguanide complexes have also been measured using the Gouy method. The complexes like all other Pd^{II} complexes are diamagnetic. Like the corresponding Ni^{II} complexes, these may also be represented by a square planar configuaration with dsp^2 hybird bonds.

In continuation of the present work it is intended to study more thoroughly the affinity of Pd^{IV} for these ligands although preliminary tests have shown that this affinity is not very strong. It is interesting to note here that Pt^{II} with which the chemical resemblance of Pd^{II} is as well-pronounced as with Ni^{II}, shows little tendency to co-ordinate with biguanides. Further work in this direction is, however, in progress.

EXPERIMENTAL

Palladium bis-*Methylbiguanidinium Sulphate*.—Fine, silky, yellowish white crystals of the complex sulphate were precipitated by the addition of sodium chloropalladite solution (equivalent to 0.5 g. Pd) to that of methylbiguanide acid sulphate (2.5 g.) in hot water (50 c.c.). The mixture was digested on the water-bath for about 15 minutes and then cooled. The crystals were first washed with water, then with alcohol and finally dried in air. The substance is sparingly soluble in water.

$$K_2PdCl_4 + 2\ \text{me-BigH}.\ H_2SO_4 = [Pd\ (\text{me-BigH})_2]SO_4 + 2KCl + 2HCl + H_2SO_4$$

(where me-BigH = $CH_3.C_2N_5H_6$, a molecule of methylbiguanide). {Found : Pd, 23.46 ; N, 30.85 ; SO_4, 21.14 ; H_2O (110°), 3.67. $[Pd(CH_3.C_2N_5H_6)_2]\ SO_4.\ H_2O$ requires Pd, 23.67 ; N, 31.06 ; SO_4, 21.30 ; H_2O, 3.99%}.

Complex Hydroxide.—Shining yellowish white crystals of the complex base were obtained by digesting the complex sulphate in aqueous suspension with NaOH. The crystals were first washed with water, then with alcohol and finally dried over $CaCl_2$ and KOH. The substance is very sparingly soluble in water. The aqueous suspension reacts alkaline to litmus. The substance on treatment with ammonium salts forms the corresponding complex salts with the liberation of ammonia. {Found : Pd, 27.91 ; N, 36.51 ; H_2O (110°), 1.82. $[Pd(CH_3C_2N_5H_6)_2]\ (OH)_2,\ 0.5\ H_2O$ requires Pd, 28.09 ; N 36.87 ; H_2O, 1.64%}.

Complex Chloride.—The complex sulphate was triturated with an equivalent quantity of barium chloride solution. The mixture was then digested on the water-bath for half an hour. The precipitated barium sulphate was filtered off. The light yellow filtrate was evaporated to a small volume and then cooled in ice when the silky yellowish white crystals of the complex chloride separated out. These were washed with ice-cold water and dried in air. The substance is fairly

soluble in water, forming a light yellow solution. It is insoluble in alcohol. The compound can also be prepared by digesting the complex base with ammonium chloride. {Found : Pd, 23.26 ; N, 30.15 ; H_2O (110°), 11.66. [Pd $(CH_3.C_2N_5H_6)_2$] Cl_2. $3H_2O$ requires Pd, 23.11 ; N, 30.32 ; H_2O, 11.69%}.

Complex Nitrate.—Silky yellowish white crystals of the nitrate were obtained by adding a solution of potassium nitrate to that of the complex chloride. This can also be prepared by digesting the complex base with ammonium nitrate. It was purified by recrystallisation from hot water. The substance is moderately soluble in water. {Found : Pd, 21.75 ; N, 34.88 ; H_2O (110°), 6.16. $[Pd(CH_3.C_2N_5H_6)_2](NO_3)_2$,$1.5H_2O$ requires Pd, 21.88 ; N, 34.45 ; H_2O, 5.54%}.

The *complex thiocyanate* was prepared by adding a strong solution of potassium thiocyanate to that of the complex chloride. It forms yellowish white silky crystals, moderately soluble in water. {Found : Pd, 21.61 ; S, 12.96. $[Pd(CH_3.C_2N_5H_6)_2](SCN)_2.2H_2O$ requires Pd, 21.83 ; S, 13.10%}.

Palladium bis-*Methylbiguanide Palladothiocyanate.*—The above described complex palladium biguanide thiocyanate on digestion with dilute hydrochloric acid (pH~2) on the water-bath for a few minutes furnished a brownish red, silky, crystalline precipitate of the complex palladium *bis*-methylbiguanide palladothiocyanate. The product is insoluble in water and alcohol.

$$2[Pd(Me\text{-}BigH)_2](SCN)_2 + 2H^+ \rightarrow [Pd(Me\text{-}BigH)_2]\,Pd(SCN)_4 + 2\ Me\text{-}BigH_2^+.$$

{Found : Pd, 31.28 ; S, 18.75.$[Pd(CH_3.C_2N_5H_6)_2]Pd(SCN)_4$ requires Pd, 31.59 ; S, 18.95%}.

Palladium bis-*Ethylbiguanide Sulphate.*—The complex sulphate was obtained in the form of yellowish white silky crystals like the corresponding methylbiguanide compound from sodium chloropalladite (equivalent to 0.5 g. Pd) and ethylbiguanide acid sulphate (2.6 g.). The compound is sparingly soluble in water. {Found : Pd, 22.12 ; N, 29.07 ; SO_4, 19.85 ; H_2O (110°), 3.95.$[Pd(EtC_2N_5H_6)_2]SO_4.H_2O$ requires Pd, 22.29 ; N, 29.25 ; SO_4, 20.05 ; H_2O, 3.76%}.

Palladium bis-*Phenylbiguanidine.*—A solution of phenylbiguanide hydrochloride 2.5 g.) in hot water (60 c.c.) was treated with one of sodium chloropalladite (equivalent to 0.5 g. Pd). A light yellow solution was obtained with the formation of the complex chloride. After digesting on the water-bath for a few minutes the mixture was made alkaline when palladium phenylbiguanidine separated out in the form of light yellow crystals. These were washed and dried as in the case of other complex bases. {Found : Pd, 23.05 ; N, 30.74. $[Pd(C_6H_5.C_2N_5H_6)_2]$ requires Pd, 23.26 ; N, 30.52%}.

The substance is insoluble in water and resembles the other complex bases in properties.

Chloride.—The complex base (2 g.) was digested on the water-bath with 1% ammonium chloride solution (100 c.c.) till the evolution of ammonia had ceased. The volume of the mixture was reduced to about 70 c.c. This was filtered and the filtrate kept overnight in the cold. The light yellow crystals of the complex chloride that separated were washed with ice-cold water and dried in air. {Found : Pd, 18.98 ; N, 25.23 ; H_2O (110°), 4.68. [Pd $(C_6H_5.C_2N_5H_6)_2$] Cl_2, $1.5H_2O$ requires Pd, 19.10 ; N, 25.06 ; H_2O,4.83%}.

The substance is moderately soluble in water and the solution turns turbid on standing. The substance is fairly soluble in alcohol giving a light yellow solution.

The corresponding complex sulphate and the nitrate were obtained as light yellow crystalline precipitate by adding a solution of the respective sodium salt to that of the complex chloride. These are sparingly soluble in cold water and fairly soluble in hot water. Their composition and analytical data are recorded in Table I.

TABLE I

Palladium ethylbiguanide :	
Base : $[Pd(C_2H_5.C_3N_5H_6)_2](OH)_2.H_2O$ Prepared by digesting the complex sulphate with alkali. Very sparingly soluble in water.	Pd, 25.66 (25.48) N, 33.26 (33.44) H_2O (120°), 4.39 (4.30)
Dehydrated sample (120°)	Pd, 26.75 (26.62)
Chloride : [X] $Cl_2.2H_2O$ Prepared by digesting the complex sulphate with barium chloride. Readily soluble in water ; light yellow solution.	Pd, 22.55 (22.62) N, 29.48 (29.68) H_2O (110°), 7.40 (7.63)
Nitrate : [X] $(NO_3)_2$ Sparingly sol. in cold water, fairly soluble in hot water.	Pd, 21.92 (21.83) N, 34.62 (34.38)
Palladium dimethylbiguanide :	
Sulphate : $[Pd(Me_2.C_3N_5H_5)_2]\ SO_4.3H_2O$ Almost insol. in cold water, very sparingly sol. in hot water.	Pd, 20.53 (20.72) SO_4, 18.67 (18.65) H_2O (110°), 9.77 (10.49)
Base : $[Pd(Me_2C_3N_5H_4)_2]0.5H_2O$ Insol. in cold water, very sparingly sol. in hot water.	Pd, 28.47 (28.70) N, 37.85 (37.66) H_2O (110°), 2.65 (2.42)
Chloride : [X] $Cl_2.2H_2O$ Fairly sol. in water ; light yellow solution.	Pd, 22.58 (22.62) N, 29.42 (29.68) H_2O (110°), 7.27 (7.63)
Natrate : [X] $(NO_3)_2.0.5H_2O$ Sparingly sol. in cold water, fairly sol. in hot water.	Pd, 21.35 (21.43) N, 33.92 (33.75) H_2O (110°), 1.85 (1.81)
Thiocyanate : [X] $(SCN)_2.1.5H_2O$ Moderately sol. in water.	Pd, 21.04 (21.01) S, 12.42 (12.61)
All the above mentioned compounds form yellowish white silky crystals.	
Palladothiocyanate : $[X]Pd(SCN)_4$ Brownish red crystals, insol. in water.	Pd, 30.12 (30.34) S, 18.06 (18.20)
Palladium phenylbiguanide :	
Sulphate : $[Pd(C_6H_5C_2N_5H_6)_2]SO_4.H_2O$	Pd, 18.42 (18.57) SO_4, 16.65 (16.70) H_2O (110°), 2.84 (3.13)
Nitrate : $[X](NO_3)_2.H_2O$	Pd, 17.84 (17.70) H_2O (110°), 3.12 (2.99)
Palladium ethylenedibiguanide :	
Base : $[Pd(Et(BigH)_2)]$ Prepared from 0.5 g. $PdCl_2$ and 2 g. of ethylenedibiguanide acid sulphate in alkaline soln. Light yellow crystals, insol. in water.	Pd, 28.94 (28.94) N, 37.82 (37.97) H_2O (110°), 9.54 (9.77)
Chloride : [X] $Cl_2.4H_2O$ Prepared by triturating the base with an equivalent quantity of HCl. Yellowish brown crystals, insol. in water.	Pd, 22.41 (22.35) N, 29.13 (29.31) Cl, 14.80 (14.87) H_2O (110°), 14.98 (14.85)
Sulphate : [X] $SO_4.3H_2O$ Prepared by triturating the base with H_2SO_4. Light yellow crystals, insol. in water.	Pd, 21.70 (21.61) N, 28.25 (28.36) SO_4, 19.47 (19.45)

N.B. Calculated analytical values are shown in parenthesis. X, wherever used in the Table, stands for the preceding complex cation.

TABLE II

Conductivity masurement (30°).
Cell constant = 1.775.

Substance.	Conc. ($M \times 10^3$)	Conductance. (mhos $\times 10^4$)	Mol. conduc. (mhos)
$[Pd(CH_3.C_2N_5H_6)_2]Cl_2.3H_2O$	2.4740	3.12	224
	4.0510	4.90	214
$[Pd(C_2H_5.C_2N_5H_6)_2]Cl_2.2H_2O$	0.9795	1.32	240
	1.9720	2.50	224
$[Pd(Me_2.C_2N_5H_6)_2]Cl_2.2H_2O$	1.5700	2.00	226
	2.0100	2.55	225
$[Pd(CH_3.C_2N_5H_6)_2]SO_4.2H_2O$	0.8964	1.08	214

Palladium bis-*Benzylbiguanide Sulphate*.—The yellowish white curdy complex sulphate was obtained by adding a solution of sodium chloropalladite (equivalent to 0.5 g. Pd) to that of benzylbiguanide acid sulphate (3.2 g.) in hot water (75 c.c.). The substance is almost insoluble in water, and sparingly soluble in hot water. {Found : Pd, 17.31 ; SO_4, 15.54 ; HO_2 (110°), 4.24. [Pd (Bz. $C_2N_5H_6)_2$]-SO_4. 1.5 H_2O requires Pd, 17.44 ; SO_4, 15.70 ; H_2O 4.42%}.

The complex *base* was obtained as very sparingly soluble yellowish white crystals by treating an alkaline solution of the biguanide with that of sodium chloropalladite and digesting the mixture on the water-bath for a few minutes. {Found : Pd, 22.12 ; N, 28.62. [Pd ($C_6H_5CH_2.C_2N_5H_5)_2$] requires Pd, 21.93 ; N, 28.77%}.

The complex *chloride* was prepared by triturating the above base with an equivalent amount of HCl (dilute). It was purified by recrystallisation from a large volume of water. The substance forms yellowish white silky crystals, very sparingly soluble in cold water and moderately soluble in hot water. It is more soluble in warm alcohol, forming a yellow solution. {Found : Pd, 17.74 ; H_2O (110°), 6,32. [Pd ($C_6H_5CH_2.C_2N_5H_6)_2$)] $Cl_2.2H_2O$ requires Pd, 17.91 ; H_2O,604%}.

The preparation and properties of other compounds along with their percentage composition are recorded in Table I.

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INFLUENCE OF CHEMICAL CONSTITUTION ON THE ROTATORY POWER OF OPTICALLY ACTIVE COMPOUNDS. PART VII. ROTATORY DISPERSION OF THE SALTS OF QUININE WITH BENZOIC, AND CHLORO-, IODO- AND NITRO-BENZOIC ACIDS (*o, m & p*)

By Maghar Singh Manhas and Sakti Prasad Banerjee

Optically active salts of quinine with benzoic, and *o*-, *m*- and *p*-isomers of chloro-, iodo- and nitro-benzoic acids have been prepared and their rotatory dispersions studied in different solvents. It is found to be 'simple' as it follows Drude's one-term equation. The role of the solvent and position isomerism with respect to the rotatory power of these compounds has been investigated. The effect of replacing the hydrogen atom by electropositive and electronegative groups on the rotatory power has also been explored.

In some of the earlier communications of this series (*Proc. Nat. Acad. Sci., India,* 1957, **26A,** 286; *J. Univ. Saugar,* 1957, **6,** 23; this *Journal,* 1959, **36,** 713) the authors have reported their results on the study of the rotatory power of several brucine salts. The present investigation is an extention of this work and includes the optically active salts of quinine with benzoic and isomeric substituted benzoic acids. The rotatory dispersion studies of these salts have been carried out in various non-aqueous solvents. The authors have also studied the effect of substituting the hydrogen atom by the electronegative chlorine and iodine atoms and electropositive nitro group in the *o*-, *m*- and *p*-positions of the quinine benzoate.

Experimental

The compounds discussed in the present communication were prepared by mixing equimolecular quantities of quinine and the different acids in absolute alcohol. The solutions thus obtained were filtered and then allowed to cool for sometime. The salts separated out on scratching and were purified by repeated recrystallisations. In some cases the salts had to be precipitated out by the addition of a small amount of sulphuric ether before recrystallisations. These compounds were generally highly soluble in chloroform, pyridine and glacial acetic acid, less so in methyl and ethyl alcohols and practically insoluble in non-polar solvents. The purity of the compound was confirmed in each case by elementary analysis (Table V).

The rotatory power determinations were made in a 2 dcm. polarimeter tube. All the observations were carried out at room temperature (approximately 30°).

Nature of Rotatory Dispersion

The rotatory dispersion of different salts of various aromatic acids with quinine has been determined in the visible region of the spectrum in various non-ionising

solvents and the results are recorded in Tables I to IV. It is found to be 'simple' as it obeys one-term Drude's equation,

$$[\alpha] = \frac{K}{\lambda^2 - \lambda^2_0}.$$

In this equation K represents the rotation constant and λ_0 is the wave-length of the dominant absorption band of its molecule in the ultraviolet region of the spectrum.

TABLE I

Quinine benzoate.

Solvent :	Pyridine	EtOH	MeOH	$CHCl_3$
Conc. (g./100 c.c.) ...	1.00	0.500	0.500	0.500
Calc. $[\alpha]$ ...	$\frac{15.73}{\lambda^2-0.0651}$	$\frac{33.36}{\lambda^2-0.0849}$	$\frac{42.47}{\lambda^2-0.0679}$	$\frac{50.64}{\lambda^2-0.0624}$
Calc. λ_0 ...	0.2551	0.2914	0.2606	0.2498
Line.	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].
Li_{6708}	-40.00°	-92.00°	-112.00°	-130.90°
Cd_{6438}	45.50	100.90	123.00	144.50
Li_{6104}	50.50	116.30	140.00	163.60
Na_{5893}	55.50	127.20	153.00	177.20
Hg_{5780}	57.50	133.60	160.00	187.20
Hg_{5461}	67.50	157.20	186.00	214.50
Cd_{5086}	81.50	191.70	224.00	258.00
Cd_{4799}	94.50	229.00	263.00	300.90
Cd_{4678}	101.50	249.00	283.00	323.60
Li_{4603}	107.50	263.60	297.00	339.00
Hg_{4358}	126.00	317.20	350.00	398.10

DISCUSSION

Effect of Solvent on the Rotatory Power

It has been emphasised by various workers (Pribram, *Ber.*, 1889, **22**, 6; Patterson *et al.*, *J. Chem. Soc.*, 1901, **79**, 167 et seq) that the solvent plays an important role in effecting the rotatory power of optically active compounds. However, no generalisation seems forthcoming as yet which can correlate the observed facts. The authors have determined the rotatory power of quinine salts under investigation in various non-ionising solvents. Table V records the values of these compounds corresponding to Hg_{5461} line.

TABLE II

Quinine chlorobenzoates.

Solvent :	Pyridine			Methyl alcohol			Ethyl alcohol			Chloroform		
Compound :	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*
Conc. (g./100 c.c.) :	1.00	1.00	1.00	0.500	0.500	0.500	0.500	0.500	1.00	0.500	0.500	0.500
Calc. α' ...	16.02	14.72	13.11	39.92	41.70	32.50	31.92	33.59	37.08	37.08	46.37	48.88
Calc. λ_0 ...	λ^2-0.0690 / 0.2627	λ^2-0.0767 / 0.2769	λ^2-0.0883 / 0.2972	λ^2-0.0726 / 0.2694	λ^2-0.0691 / 0.2629	λ^2-0.0884 / 0.2973	λ^2-0.078 / 0.2793	λ^2-0.0761 / 0.2759	λ^2-0.0664 / 0.2577	λ^2-0.0664 / 0.257?	λ^2-0.0612 / 0.2474	λ^2-0.0579 / 0.2406
Line.	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs [α].
Li_{6708}	-41.00°	-38.00°	-36.50°	-106.00°	-109.00°	-90.00°	-86.00°	-90.00°	-96.00°	-97.00°	-119.00°	-125.00°
Cd_{6438}	45.50	44.00	40.00	116.00	121.00	100.00	95.00	100.00	106.00	107.00	131.00	137.00
Li_{6104}	51.00	49.50	46.00	134.00	137.00	114.00	108.00	112.00	120.00	121.00	150.00	156.00
Na_{5893}	56.00	53.00	50.50	145.00	150.00	126.00	117.00	124.00	132.00	132.00	162.00	169.00
Hg_{5780}	60.50	57.00	53.50	153.00	157.00	131.00	125.00	130.00	138.00	139.00	170.00	170.00
Hg_{5461}	70.00	66.50	62.50	177.00	182.00	155.00	145.00	151.00	160.00	160.00	196.00	203.00
Cd_{5086}	84.50	81.00	77.00	214.00	220.00	191.00	177.00	184.00	192.00	191.00	235.00	243.00
Cd_{4799}	98.00	96.00	91.00	253.00	259.00	229.00	208.00	218.00	228.00	226.00	274.00	283.00
Cd_{4678}	107.50	103.50	100.50	273.00	278.00	249.00	227.00	235.00	244.00	243.00	294.00	303.00
Li_{4602}	112.50	107.50	106.00	287.00	292.00	263.00	238.00	245.00	256.00	256.00	308.00	318.00
Hg_{4358}	132.50	130.00	129.00	340.00	354.00	320.00	285.00	295.00	300.00	300.00	360.00	370.00

TABLE III

Quinine iodobenzoates.

Solvent :	Pyridine			Methyl alcohol			Ethyl alcohol			Chloroform		
Compound :	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*	*o-*	*m-*	*p-*
Conc. (g./100 c.c.) :	1.00	1.00	1.00	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500	0.500
Calc. [α]	11.61	9.965	10.89	34.73	30.70	32.11	30.70	28.89	31.75	36..9	40.71	38.89
	λ^3-0.0964	λ^3-0.0951	λ^3-0.091	λ^3-0.0681	λ^3-0.0621	λ^3-0.0688	λ^3-0.0625	λ^3-0.0575	λ^3-0.063	λ^3-0.0632	λ^3-0.0713	λ^3-0.0625
λ_0	0.3105	0.3084	0.3017	0.2610	0.2492	0.2623	0.2492	0.2398	0.2510	0.2514	0.2670	0.2500
Line.	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].
Li_{6708}	-33.00°	-.6.00°	-31.00°	-90.00°	-79.00°	-84.00°	-79.00°	-74.00°	-81 00°	-94.00°	-107.00°	-101.00°
Cd_{6438}	36.00	30.00	33.50	100.00	87.00	92.00	87.00	81.00	90.00	104.00	119.00	112.00
Li_{6104}	44.00	36.00	38.50	114.00	98.00	106.00	99.00	90.00	103.00	117.00	135.00	125.00
Na_{5893}	46.50	39.50	42.00	125.00	108.00	115.00	108.00	100.00	112.00	128.00	148.00	137.00
Hg_{5708}	49.50	42.00	45.00	131.00	113.00	121.00	111.00	104.00	117.00	134.00	155.00	143.00
Hg_{5461}	57.50	49.50	52.50	151.00	130.00	140.00	130.00	120.00	135.00	154.00	179.00	165.00
Cd_{5085}	70.50	63.00	65.50	182.00	157.00	169.00	156.00	144.00	162.00	186.00	217.00	198.00
Cd_{4799}	85.50	74.00	78.50	214.00	182.00	198.00	184.00	167.00	190.00	216.00	256.00	232.00
Cd_{4678}	97.50	81.00	85.00	230.00	196.00	214.00	196.00	179.00	201.00	233.00	276.00	249.00
Li_{4602}	100.50	85.00	92.00	242.00	205.00	225.00	205.00	188.00	211.00	244.00	290.00	261.00
Hg_{4358}	124.00	105.00	110.00	285.00	240.00	265.00	240.00	218.00	250.00	286.00	343.00	305.00

TABLE IV

Quinine nitrobenzoates.

Solvent :	Pyridine			Methyl alcohol			Chloroform		
Compound :	*o*-	*m*-	*p*-	*o*-	*m*-	*p*-	*o*-	*m*-	*p*-
Conc. (g./100 c.c.) :	1.00	1.00	1.00	0.500	0.500	0.500	1.00	0.500	0.500
Calc. [α]	14.45	16.19	14.00	34.09	35.71	33.33	41.62	49.09	42.94
Calc. λ_0	λ^2-0.071 / 0.2665	λ^2-0.064 / 0.2530	λ^2-0.0724 / 0.2691	λ^2-0.0851 / 0.2917	λ^2-0.0818 / 0.2860	λ^2-0.0835 / 0.2941	λ^2-0.0744 / 0.2728	λ^2-0.0657 / 0.2563	λ^2-0.0655 / 0.2559
Line.	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs.[α].	Obs [α].	Obs.[α].
Li_{6708}	-38.00°	-41.50°	-37.00°	-93.00°	-97.00°	-91.00°	-111.00°	-128.00°	-112.00°
Cd_{6438}	42.00	47.00	41.00	104.00	107.00	101.00	124.00	141.00	123.00
Li_{6104}	47.00	52.50	46.00	118.00	123.00	115.00	140.00	160.00	140.00
Na_{5893}	52.00	57.00	51.00	131.00	135.00	127.00	153.00	175.00	153.00
Hg_{5780}	55.00	60.00	53.50	137.00	142.00	135.00	160.00	183.00	160.00
Hg_{5461}	64.00	70.00	62.00	160.00	165.00	157.00	186.00	211.00	184.00
Cd_{5086}	77.00	83.50	75.00	196.00	201.00	193.00	225.00	254.00	222.00
Cd_{4799}	90.00	95.50	88.50	234.00	240.00	232.00	266.00	298.00	260.00
Cd_{4678}	97.00	104.50	95.50	255.00	260.00	251.00	288.00	320.00	280.00
Li_{4603}	104.00	109.00	102.00	270.00	275.00	266.00	301.00	336.00	293.00
Hg_{4358}	121.00	128.50	119.00	325.00	330.00	321.00	360.00	395.00	345.00

TABLE V

	Quinine salts.	M.P.	% Nitrogen. Found.	% Nitrogen. Calc.	$[\alpha]^{30}_{5461}$ $CHCl_3$ (5.2)*	Pyridine. (12.4)*	EtOH. (23.8)*	MeOH. (31.2)*
1.	Benzoate	176-77° (d)	6.20	6.28	214.50 †(50.64)	67.50 †(15.73)	157.20 †(33.36)	186.00 †(42.74)
2.	*o*-Chlorobenzoate	154-56°	5.60	5.83	160.00 (37.08)	70.00 (16.02)	145.00 (31.92)	177.00 (39.92)
3.	*m*- „	152°	5.93	„	196.00 (45.91)	66.50 (14.72)	151.00 (33.59)	182.00 (41.70)
4.	*p*- „	190-91°	5.75	„	203.00 (48.88)	62.50 (13.11)	160.00 (37.08)	155.00 (32.50)
5.	*o*-Iodobenzoate	194°	4.80	4.88	154.00 (36.29)	57.50 (11.61)	130.00 (30.70)	151.00 (34.73)
6.	*m*- „	119°	4.69	„	179.00 (40.71)	49.50 (9.965)	120.00 (28.89)	130.00 (30.70)
7.	*p*- „	168-69°	5.15	„	165.00 (38.89)	52.50 (10.89)	135.00 (31.75)	140.00 (32.11)
8.	*o*-Nitrobenzoate	160°	8.50	8.55	186.00 (41.62)	64.50 (14.45)	..	160.00 (34.09)
9.	*m*- „	194-95°	8.30	„	211.00 (49.09)	70.00 (16.19)	..	165.00 (34.85)
10.	*p*- „	200-201°	8.43	„	184.00 (42.94)	62.00 (14.00)	..	157.00 (33.72)

* The figures in parenthesis refer to the values of the dielectric constants of the solvents.

† The figures in brackets refer to the rotation constants, *K*.

From a study of this table it will be observed that the sequence of decreasing rotatory power in various solvents runs parallel to the decreasing values of the dielectric constants of the solvents except for minor variations.

Further it will be noted from the same table that excepting for quinine *o*-chlorobenzoate, all other quinine salts exhibit the maximum rotation in chloroform. Our similar investigations with brucine salts in different solvents, in which the observations were made, indicated that these salts showed the maximum rotation in pyridine. Thus it will be evident that besides the dielectric constants or other similar physical characteristics which have hitherto been made the basis of comparison of the rotatory power, the constitution of the optically active compound and that of the solvent in relation to each other also appear to have an important bearing in determining the rotatory effect of the solvent. Further work is being carried out.

Effect of Position Isomerism on the Rotatory Power

In Table VI the orders of the specific rotatory power, $[\alpha]^{30}_{5461}$, for the position isomerides in different solvents are given. The orders of K, the rotation constants, are also given for the purpose of comparison.

On comparing the values of $[\alpha]^{30}_{5461}$ in chloroform, the sequence of position isomerides is $o<m<p<un$ for quinine chlorobenzoates $o<p<m<un$ for quinine iodobenzoates and $p<o<m<un$ for quinine nitrobenzoates. Excepting for quinine chlorobenzoates these results do not agree with Frankland's 'lever arm' hypothesis (*J. Chem. Soc.*, 1896, **69,** 1583). However, excepting for quinine nitrobenzoates, the above sequences are in agreement with Cohen's rule (*ibid.*, 1903, **38,** 1214, et seq) which lays down that the *ortho* substituent has the greatest effect in diminishing or increasing the rotation and that substituents in the *meta* and more especially in the *para* position have a very subordinate effect. When the values of K are compared, the order in chloroform is $o<m<p<un$ for chlorobenzoates, $o<p<m<un$ for iodobenzoates and $o<p<m<un$ for nitrobenzoates. These results do not agree with Frankland's 'lever-arm' hypothesis excepting for quinine chlorobenzoates, but agree with Cohen's rule.

In pyridine the order for $[\alpha]^{30}_{5461}$ and K is $m<p<o<un$ for iodobenzoates, $p<m<un<o$ for chlorobenzoates and $p<o<un<m$ for nitrobenzoates. These results, excepting for quinine chlorobenzoates, do not agree with either Frankland's hypothesis or with Cohen's rule.

In ethyl alcohol the order is $m<o<p<un$ for iodobenzoates and $o<m<un<p$ for chlorobenzoates. Similar results follow when a comparison is made for the values of K. In quinine chlorobenzoates the rules of both Frankland and Cohen are followed but the iodobenzoates do not respond to any one of them.

In methyl alcohol the order is $m<p<o<un$ for iodobenzoates, $p<o<m<un$ for chlorobenzoates and $p<o<m<un$ for nitrobenzoates. Comparison of the values of K also provides identical results. These results agree neither with Frankland's hypothesis nor with Cohen's rule.

Effect of Substituent Groups on the Rotatory Power

Rule (*J. Chem. Soc.*, 1924, **125**, 1122) has shown that the arrangement of groups according to their polarities, in general, follows the following order :

OH^-, Cl, Br, I, NH_2, C_2H_5, CH_3, H^+, COOH, CHO, $COCH_3$, CN, NO_2^+

In Table VI values of $[\alpha]^{30}_{5461}$ in different solvents are given. The values of K, the rotation constant, as above defined, are for the sake of comparison.

TABLE VI

Solvent	Chlorobenzoates. $[\alpha]^{30}_{5461}$.	Chlorobenzoates. K.	Iodobenzoates. $[\alpha]^{30}_{5461}$.	Iodobenzoates. K.
$CHCl_3$	$o<m<p<un$	$o<m<p<un$	$o<p<m<un$	$o<p<m<un$
Pyridine	$p<m<un<o$	$p<m<un<o$	$m<p<o<un$	$m<p<o<un$
EtOH	$o<m<un<p$	$o<m<un<p$	$m<o<p<un$	$m<o<p<un$
MeOH	$p<o<m<un$	$p<o<m<un$	$m<p<o<un$	$m<p<o<un$
	Nitrobenzoates.			
$CHCl_3$	$p<o<m<un$	$o<p<m<un$		
Pyridine	$p<o<un<m$	$p<o<un<m$		
EtOH	....	....		
MeOH	$p<o<m<un$	$p<o<m<un$		

Ortho-substitution.—On comparing the values of $[\alpha]^{30}_{5461}$ in chloroform it is found that the groups iodo, chloro and nitro cause a decrease in the rotatory power in the order : $I<Cl<NO_2<H$. Similar order is followed on comparing the values of K. This is in agreement with polar series, excepting NO_2.

In pyridine the order of specific rotatory power is $I<NO_2<H<Cl$. Similar order is followed on comparing the values of K. Here the groups Cl and NO_2 do not behave in conformity with the polar series.

Comparison of the values of $[\alpha]^{30}_{5461}$ and K in ethyl alcohol gives the order of increasing rotatory power as $I<Cl<H$. The introduction of negative Cl and I groups depresses the rotation in conformity with the polar series.

In methyl alcohol the order is $I<NO_2<Cl<H$. Here it is found that the replacement of H by Cl and I atoms leads to a lowering of the rotatory power in conformity with the polar order. The NO_2 group, however, stands out in its behaviour.

Meta-substitution.—The comparison of the values of $[\alpha]^{30}_{5461}$ and K in chloroform gives the order of decreasing rotatory power as $I<Cl<NO_2<H$. Here again the order is in conformity with the polar effect of the substituent groups excepting NO_2.

In pyridine the order of decreasing rotatory power or of absolute rotation constant is $I<Cl<H<NO_2$. This is in agreement with the polar series.

In ethyl alcohol the order is $I<Cl<H$. Thus the introduction of electronegative Cl and I atoms in place of H depresses the rotatory power in conformity with the polar series.

In methyl alcohol the order has been found to be $I<NO_2<H<Cl$. Here the groups NO_2 and Cl do not agree with the above mentioned order.

Para-substitution.—On comparing the values of $[\alpha]^{30}_{5461}$ and K in chloroform, the order is $I<NO_2<Cl<H$. With the exception of NO_2 this sequence is in agreement with the polar series.

In pyridine, where the order is $I<NO_2<Cl<H$, the nitro group stands out of the polar series. In ethyl alcohol the order for $[\alpha]^{30}_{5461}$ and K is $I<H<Cl$. With the exception of Cl it agrees with polar series. In methyl alcohol the nitro group falls out where the order is $I<Cl<NO_2<H$.

From the above results it can be concluded that on the replacement of H atom by negative groups, the rotation is depressed in most of the cases which is in agreement with the polar series. However, the NO_2 group has been found to behave abnormally in so far as its rotatory effect on the optically active quinine salts is concerned.

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SYNTHESIS OF SOME NEW FURFURYLIDENE COMPOUNDS

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Furfuraldehyde has been condensed with malonanilic acid, malon-*o*-, -*m*- and -*p*-toluidic acids and also with *n*-heptamide, cinnamamide and phenylacetamide. The acids yielded furfurylidene-malonanilic and furfurylidene-malon-*o*-, -*m*- and -*p*-toluidic acids. Pyridine in traces has been found to be a very good catalyst in these condensations. The amides afford the corresponding furfurylidene-*bis*-amides.

Condensation of furfuraldehyde with reactive methylene compounds and with acid amides yielding furfurylidene derivatives has been reported by various workers (cf. Dalal and Dutt, this *Journal*, 1932, **9**, 309; Beaucourt, *Monatsh.*, 1928, **49**, 1). The amides used by Beaucourt (*loc. cit.*) were acetamide, propionamide butyramide and benzamide. The product in each case was the corresponding furfurylidene-*bis*-amide and the yield ranged from 30 to 40%. With formamide the product was an intractable resin. Furfuraldehyde and certain aryl sulphonamides were condensed by Lichtenberger *et al.* (*Bull. Soc. Chim.*, 1955, 669).

The condensation of furfural with malonanilic acid and malon-*o*-, -*m*- and -*p*-toluidic acids and also with heptamide, cinnamamide and phenylacetamide is reported herein. Malonanilic acid and the three malon-toluidic acids were prepared by the method of Chattaway and Olmstead (*J. Chem. Soc.*, 1910, **97**, 939). Cinnamamide and phenylacetamide were prepared from the corresponding acids through their acid chlorides.

In condensations with malonanilic acid and the three malon-toluidic acids only the corresponding furfurylidene-malonanilic acid or -toluidic acid was obtained; in no case could the corresponding furfuracrylanilide or -toluidide be isolated. Use of carbon dioxide as an inert atmosphere to minimise resinification of aldehyde had no marked effect. But when a trace of pyridine was used as a condensing agent, there was marked increase in the yield of products.

Condensation of formamide, acetamide and benzamide were repeated and Beaucourt's (*loc. cit.*) observations were confirmed. Heptamide, phenylacetamide and cinnamamide condensed very well with furfural and yielded the corresponding *bis*-amides which were all white crystalline compounds. Use of pyridine in these reactions did not in any way help.

Experimental

Furfurylidene-malonanilic Acid.—A mixture of malonanilic acid (1.5 g.) and furfuraldehyde (0.8 g.) was heated at 100° in a 50 c.c. r.b. flask. The mixture melted immediately and slowly darkened in colour. After heating for about 30 minutes the liquid mass started solidifying. Heating was continued for another 3 hours after which the brownish black solid was extracted with a strong solution of sodium bicarbonate, leaving behind a lot of black resinous matter. The alkali extract was filtered and to it HCl (conc.) was added in excess. The yellowish grey precipitate obtained was filtered and recrystallised twice from

dilute alcohol, m.p. 221° (decomp.), yield 0.95 g. (44.2%). (Found : N, 5.31. $C_{14}H_{11}O_4N$ requires N, 5.45%).

When heating was done for one hour only to minimise the formation of resinous matter, the yield was poor (19%). When heating at 100° was done for 1 hour with addition of a trace of pyridine (0.15 *M*), 62.5% yield of furfurylidene-malonanilic acid was obtained.

Furfurylidene-malon-o-toluidic Acid.—Furfural (0.96 g.) and malon-*o*-toluidic acid (1.93 g.) were mixed and heated at 100° for 2 hours. The mixture fused to a brownish melt which gradually darkened in colour and finally set to a solid. On extraction in the manner described before and after repeated recrystallisation from dilute alcohol, 1.6 g. of furfurylidene-malon-*o*-toluidic acid was obtained (57.7% yield). The crystals were pale yellowish brown in colour and needle-shaped, m.p. 197° (decomp.). Use of pyridine as a catalyst raised the yield to 67.5%. (Found : N, 5.1. $C_{15}H_{13}O_4N$ requires N, 5.16%).

*Furfurylidene-malon-*m-*toluidic acid* was prepared in the same manner, as mentioned above, by heating equimolecular quantities of furfural and malon-*m*-toluidic acid at 100° for 4 hours. After repeated trials it was crystallised from very dilute alcohol, m.p. 179° (decomp.). The yield ranged from 24 to 30% in various experiments; with a trace of pyridine as a catalyst, the yield was raised to 50%. (Found : N. 5.54. $C_{15}H_{13}O_4N$ requires N, 5.16%).

*Furfurylidene-malon-*p-*toluidic acid* was obtained similarly on heating a mixture of furfural (1.1 g.) and the corresponding acid (2.1 g.) at 100° for 2 hours in 39% yield. The yield rose to 60% when a trace of pyridine was used. It was crystallised from dilute alcohol in pale yellowish brown crystals, m.p. 210° (decomp.). (Found : N. 5.5. $C_{15}H_{13}O_4N$ requires N, 5.16%).

*Furfurylidene-*bis-*heptamide.*—A mixture of furfuraldehyde (0.96 g.) and heptamide (2.6 g.) was heated in a boiling water-bath in an atmosphere of carbon dioxide. The mixture which first melted to a clear liquid set to a dark brown solid. After heating for 3 hours, the mass was extracted with water to remove unchanged heptamide. The residue was washed with ether and crystallised from alcohol as a white lustrous crystalline product, m.p. 136°, yield 2.08 g. (62%). (Found : N, 8.69. $C_{19}H_{32}O_3N_2$ requires N, 8.33%).

*Furfurylidene-*bis-*cinnamamide* was obtained by heating a mixture of furfuraldehyde (0.48 g.) and cinnamamide (1.47 g.) for 3 hours at 100°. The solid mass left was first extracted with ether and the residue was crystallised from alcohol, m.p. 225°, yield 0.63 g. (34%). (Found : N, 7.4. $C_{23}H_{20}O_3N_2$ requires N, 7.53%).

*Furfurylidene-*bis-*phenylacetamide.*—Furfuraldehyde (0.96 g.) and phenylacetamide (2.8 g.) and absolute alcohol (3 c.c.) were mixed and heated at 115° for 4 hours. Alcohol was added to enable the components to mix better. After heating the mass was extracted with hot water to remove the unchanged amide and then the residue was crystallised from alcohol as a white crystalline product, m.p. 225°, yield 0.73 g. (21%). (Found : N, 8.1. $C_{21}H_{20}O_3N_2$ requires N, 8.04%).

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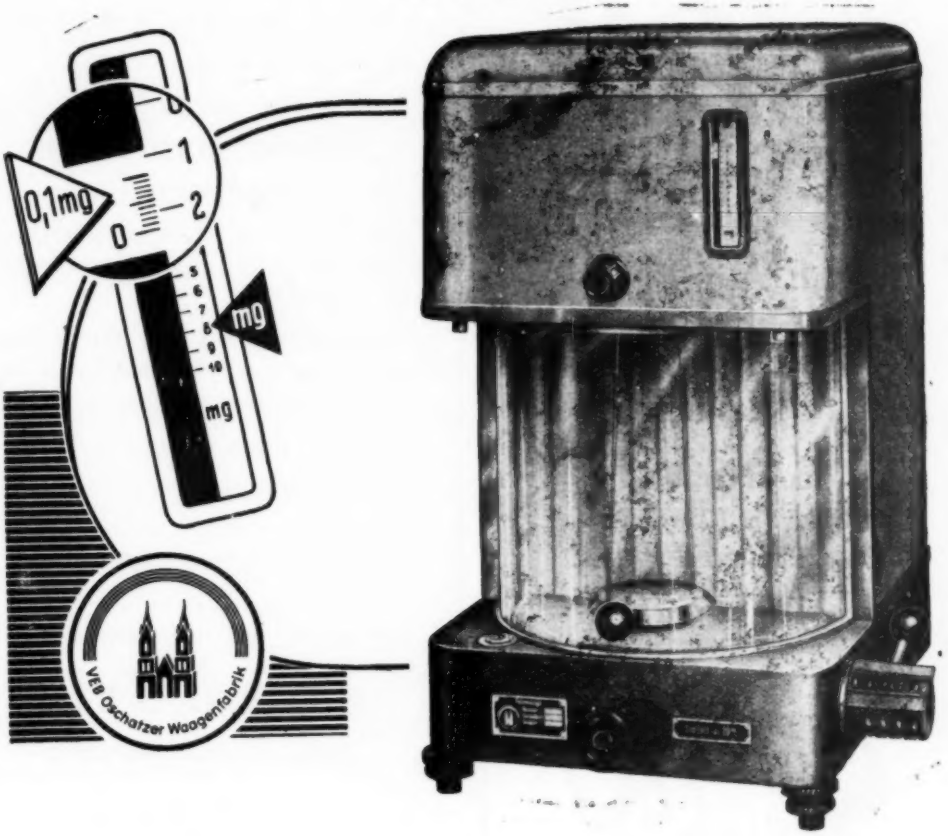

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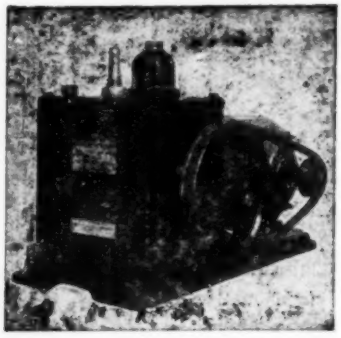

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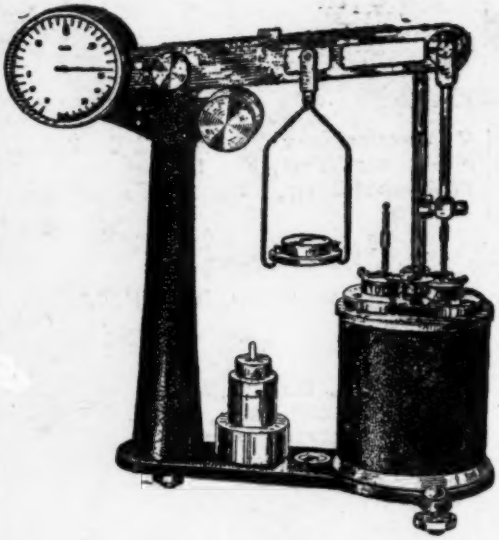

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